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The Microwave Spectrum, Dipole Moment and Low Frequency Vibrational States for Phosphabenzene

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The microwave spectrum of the ground vibrational state and seven low-frequency vibrational states for phosphabenzene (C_5H_5P) have been assigned. The small positive inertial defect and the alternation of intensities due to nuclear spin statistics for the ground state confirm a plannar structure with C_{2v} symmetry. A PC bond distance of 1.70–1.73 Å and ⟨CPC of 101°–104° were estimated based on plausible assumptions for the other ring parameters. Four low-frequency fundamental modes of vibration were identified and vibrational assignments discussed. The nuclear spin statistics indicate that three of these modes were antisymmetric to the C_2 axis while one mode was symmetric. The dipole moment has been determined as 1.54 ± 0.02 D.

INTRODUCTION

Although benzene and pyridine are familar to all chemists the phosphorus analog called phosphabenzene (phosphorin) has only recently been synthesized (*1*). A small amount of the material was available for the investigation of its microwave spectrum. The original purpose of the study was to determine the structure and dipole moment of phosphabenzene in order to elucidate the extent of aromaticity. While the dipole moment was evaluated, the structural investigation was less successful since data on the less abundant isotopic species could not be obtained. However, the symmetry and planarity of the compound have been established and some information on the PC bound length and CPC angle was obtained. In addition a rich vibrational satellite spectrum was observed and assigned. This has provided information about the symmetries, frequencies and atom motions for four of the lowest modes of vibration.

EXPERIMENTAL

The transitions were measured at room temperature with a Stark-modulated spectrometer (*2*). The assignment of the ground state and the two strongest vibrational satellites were made by observing the Stark effects using oscilloscope display. The weaker vibrational satellites' transitions were assigned from recorder traces obtained at several voltages. The uncertainties in the frequency measurements were estimated as ±0.25 MHz. This range includes the weak

vibrational satellite transitions for which it was difficult to reliably locate the center frequency.

The compound was prepared by the reaction of 1,4-dihydro-1,1-dibutyl stannabenzene with phosphorus tribromide (*1*). The synthesis was not efficient for the preparation of enriched isotopic species, which made a complete structure determination contingent upon assigning ^{13}C species in natural abundance. Based on the intensities of the normal isotopic species, these transitions were estimated to be beyond the sensitivity of the spectrometer. An unsuccessful search was made for them using recorder techniques and a computer of average transients. The search for weaker lines was handicapped by the tendency of the compound to be quickly absorbed on the cell walls.

Intensity measurements were made several ways (*3*). Some information was obtained from the recorder traces. These data were useful for establishing the nuclear spin statistics, particularly in those regions where transitions of different symmetry fell close together. The traces were somewhat less useful for estimating vibrational frequencies due to incomplete modulation, Stark lobe interference and the intrinsic low intensity of the higher vibrational states. Only the two lowest vibrations were intense enough for quantitative relative intensity measurements. Besides estimating the relative intensities from the traces of several frequency regions, two transitions ($4_{22} \rightarrow 5_{23}$ and $4_{31} \rightarrow 5_{32}$) were studied by using oscillosope display on the Michigan spectrometer and by the nonsaturation technique on the Hewlett–Packard spectrometer at Michigan State University. The uncertainty estimates for the vibrational frequencies were nevertheless large due to a scatter in the data from the various measurements.

The dipole moment was determined from Stark shift measurements by using a precision dc voltage source (*4*) (Fluke, Model 413B). The effective guide spacing was determined using the $1 \rightarrow 2$ transition of OCS, $\mu = 0.7152$ D (*5*).

ANALYSIS AND DISCUSSION

Ground state spectrum and structure. The transitions that were assigned for the ground vibrational state are listed in Table I. Only *a* type transitions were observed. The derived rotational constants and moments of inertia are listed in Table III. The rotational constants were obtained from a least-squares fit of the observed transitions. The uncertainties listed are twice the standard deviations.

Phosphabenzene is expected to be a planar molecule with the *a* inertial axis being the C_2 symmetry axis. Because there are two pairs of equivalent hydrogen atoms, a 10:6 alternation of intensities is expected. The levels for which the K value in the prolate limit is even will have the higher nuclear spin statistical weight. This alternation in intensity was clearly apparent for the closely spaced $6_{06} \rightarrow 7_{07}$ and $6_{16} \rightarrow 7_{17}$ transitions and the $7_{07} \rightarrow 8_{08}$ and $7_{17} \rightarrow 8_{18}$ transitions.

Support for a planar conformation is obtained from the value of the inertial defect for the ground state. $I_c - I_b - I_a$ for phosphabenzene is 0.052 μA^2. This

TABLE I

MEASURED FREQUENCIES FOR PHOSPHABENZENE (MHz)

Transition	Ground state		$V_a = 1$ (antisym.)		$V_b = 1$ (sym)		$V_c = 1$ (antisym)	
	obsd	$\Delta\nu$[a]	obsd	$\Delta\nu$	obs.	$\Delta\nu$	obsd	$\Delta\nu$
$3_{12} \rightarrow 4_{13}$	23380.36	0.05			23388.95	0.02		
$3_{22} \rightarrow 4_{23}$	21837.72	0.05	21840.80	0.18				
$4_{04} \rightarrow 5_{05}$	22912.49	0.07	22926.76	0.09	22930.87	−0.09		
$4_{14} \rightarrow 5_{15}$	22850.24	−0.02	22864.68	0.14				
$4_{22} \rightarrow 5_{23}$	31257.95	−0.05	31252.15	−0.40	31271.05	0.05	31273.51	−0.04
$4_{31} \rightarrow 5_{32}$	31207.09	−0.00	31200.06	0.14	31228.97	−0.03	31236.05	0.00
$5_{05} \rightarrow 6_{06}$	27045.58	−0.03	27063.00	−0.65	27069.14	0.58	27066.20	−0.39
$5_{15} \rightarrow 6_{16}$	27028.84	−0.03	27046.86	0.02	27051.55	−0.41	27050.15	0.07
$5_{14} \rightarrow 6_{15}$	31478.47	−0.02	31487.26	0.07	31493.06	−0.04	31490.63	0.02
$5_{24} \rightarrow 6_{25}$	31034.70	0.01	31043.75	0.06	31053.16	0.00		
$6_{06} \rightarrow 7_{07}$	31196.57	−0.05	31218.54	0.12	31224.00	−0.01	31221.55	−0.18
$6_{16} \rightarrow 7_{17}$	31192.44	0.04	31214.36	0.16	31219.87	0.01	31217.60	0.00
$6_{15} \rightarrow 7_{16}$	35471.74	−0.01	35484.57	0.16	35491.72	−0.08	35489.29	−0.08
$6_{25} \rightarrow 7_{26}$	35315.55	0.01	35328.30	0.09	35337.38	0.00	35335.90	0.17
$7_{07} \rightarrow 8_{08}$	35352.94	−0.03	35378.47	−0.07	35384.76	0.00	35382.30	0.16
$7_{17} \rightarrow 8_{18}$	35351.97	0.00	35377.43	−0.10	35383.65	−0.12	35381.31	0.15

[a] $\Delta\nu = \nu$ (observed) $- \nu$ (calculated).

is in the range expected for a planar conformation and can be compared with other compounds containing aromatic rings (*6*): pyridine, 0.032 μA^2; fluorobenzene, 0.027 μA^2; benzonitrile, 0.073 μA^2 and furan 0.048 μA^2. By analogy with these compounds and from the regularity of the vibrational satellite data described below, the expected planar configuration is indicated.

There are five structural parameters which define the ring geometry for phosphabenzene. It is possible to estimate two of these parameters using the I_a and I_b moments of inertia and assumptions for the other parameters and the positions of the hydrogens. These assumptions were guided by the structural parameters of other aromatic compounds and from those determined from X-ray investigations of 1,5-dimethyl, 3-phenyl phosphabenzene (I), 1,1-dimethoxy-2,4,6-triphenylphosphabenzene (II) and 2-*t*-butyl-4-aryl-5,6 dihydronaptho-1,2-phosphorin (III) (*7–9*). The CH bonds were assumed to be 1.08 Å and to bisect their adjacent ring angles. The two CC bounds were set at 1.40 Å; while $< C_2C_3C_4 = 122°$ and $< C_1C_2C_3 = 123.6°$ were assumed. This gave the following results: d(PC) = 1.727 Å $\langle C_1PC_5 = 101.1°$ and $< PC_1C_2 = 125°$. This ring structure is nearly identical to that obtained for I except for the 2° larger CPC angle in the substituted phosphabenzene. The PC bond distance is also close to that in II although the PCC angle was larger (107°) and $< C_1C_2C_3$ was smaller (120°) in that compound. In III, d(PC) was 1.75 Å and < CPC was 103°.

The meaning of the derived parameters must be qualified since they will vary

TABLE II

MEASURED FREQUENCIES FOR PHOSPHABENZENE (MHz)

Transition	$V_d = 1$ (antisym.)		$V_a = 2$ (sym.)		$V_b = 2$ (sym)		$V_a = V_b = 1$ (antisym.)	
	obsd	$\Delta\nu$	obsd	$\Delta\nu$	obsd	$\Delta\nu$	obsd	$\Delta\nu$
$4_{22} \rightarrow 5_{23}$	31260.49	−0.09	31247.41	0.06	31283.51	0.08	31266.29	0.00
$4_{31} \rightarrow 5_{32}$			31192.60	−0.03				
$5_{05} \rightarrow 6_{06}$	27055.24	−0.24	27081.73	0.12	27090.97	0.17	27086.64	0.16
$5_{15} \rightarrow 6_{16}$	27038.75	0.17	27064.24	−0.55	27074.25	−0.15	27069.69	−0.19
$5_{14} \rightarrow 6_{15}$	31488.10	−0.06	31496.14	−0.07	31507.21	0.13	31502.00	0.00
$5_{24} \rightarrow 6_{25}$	31043.11	0.29			31070.80	−0.14		
$6_{06} \rightarrow 7_{07}$			31240.20	0.09				
$6_{15} \rightarrow 7_{16}$	35482.70	−0.06						
$6_{25} \rightarrow 7_{26}$	35325.80	0.02	35341.10	0.06	35358.25	−0.18		
$7_{07} \rightarrow 8_{08}$	35366.24	0.01	35404.04	0.09	35415.58	−0.01	35410.09	−0.02
$7_{17} \rightarrow 8_{18}$	35365.17	−0.05	35403.08	0.14	35414.73	0.11	35409.16	0.04

as the assumptions involving the carbon atoms are changed. In order to obtain longer PC bonds with our data, the CC bonds would have to be shortened below values reported for benzene derivatives. This suggests that a value of 1.73 Å as an upper limit for the PC bond length in phosphabenzene. A lower limit of 1.70 Å can be set by assuming that the CC bonds will not be larger than 1.44 Å (about 0.04–0.05 Å longer than in typical benzene derivatives, pyridine and the substituted phosphabenzenes). Hence, our data are most consistent with a PC bond of 1.70–1.73 Å and $<$CPC of 101°–104°. This PC bond length is between that found in $(CH_3)_3P$ (1.843 Å) and the double bond in $(C_6H_5)_3P = CH_2$ (1.66 Å) (*10, 11*).

Vibrational satellite spectra. The ground state transitions were accompanied by a number of weaker transitions originating from excited vibrational states. Seven states were identified based on their rigid rotor frequency fit and their Stark effects. The assigned rotational transitions are in Tables I and II. The rotational constants derived by a least-square fit and the inertial defects are listed in Table III.

From intensities and the changes in rotational constants, it was concluded that these vibrational satellites arose from four fundamental modes of vibration. The spectra were characterized by two intense satellites, ν_a and ν_b, and two much weaker states, ν_c and ν_d. The other states observed were $2\nu_a$, $2\nu_b$ and several transitions from $\nu_a + \nu_b$.

The transitions, $7_{07} \rightarrow 7_{08}$ and $7_{17} \rightarrow 7_{18}$, are separated by about 1 MHz. The intensities of these transitions were used to determine whether the spin statistics were the same or reversed from the ground state. States having the same spin statistics as the ground state were ν_b, $2\nu_b$ and $2\nu_a$. The remaining states showed a reversal. Hence, it was concluded that ν_a, ν_c and ν_d are fundamental modes antisymmetric to the C_2 axis while ν_b is symmetric.

TABLE III

ROTATIONAL CONSTANTS (MHz), MOMENTS OF INERTIA (μÅ^2) AND INERTIAL DEFECTS (μÅ^2) FOR PHOSPHABENZENE

	A	B	C	I_a	I_b	I_c	Δ[a]
Ground state	5113.93	3505.54	2079.39	98.8234	144.1649	243.0405	0.0522
	±0.04	±0.01	±0.01				
$V_a = 1$	5109.74	3504.03	2081.27	98.9044	144.2270	242.8210	−0.3104
	±0.26	±0.04	±0.02				
$V_b = 1$	5108.82	3506.89	2081.57	98.9223	144.1096	242.7860	−0.2459
	±0.22	±0.04	±0.02				
$V_c = 1$	5107.49	3507.49	2081.40	98.9480	144.0849	242.8061	−0.2268
	±0.20	±0.03	±0.02				
$V_d = 1$	5115.47	3505.38	2080.25	98.7939	144.1714	242.9402	−0.0251
	±0.28	±0.06	±0.02				
$V_a = 2$	5105.87	3502.56	2083.13	98.9793	144.2878	242.6037	−0.6634
	±0.30	±0.05	±0.02				
$V_b = 2$	5103.72	3508.18	2083.69	99.0211	144.0563	242.5388	−0.5386
	±0.30	±0.06	±0.02				
$V_a = V_b = 1$	5104.80	3505.50	2083.43	99.0001	144.1666	242.5681	−0.5995
	±0.30	±0.05	±0.02				

[a] $\Delta = I_c - I_b - I_a$; conversion factor: 505376 MHz·μÅ^2.

The vibrational frequencies of the two lowest modes were estimated by measuring their intensities relative to the ground state as described in the experimental section. This gave the values, $\nu_a = 290 \pm 40$ cm^{-1} and $\nu_b = 325 \pm 40$ cm^{-1}. The remaining five states were estimated to lie in the range 450–650 cm^{-1}. They were too weak, however, to obtain more meaningful vibrational frequencies except that ν_c was noted to have a lower frequency than ν_d. Although no ir data in this region are yet available for comparison, we plan a complete study of the vibrational spectrum.

Some assignments of these modes are suggested by correlation with the low frequency modes in pyridine (*12*, *13*). The two lowest modes in pyridine, $\nu_{16a}(A_2)$, 374 cm^{-1} and $\nu_{16b}(B_2)$ 304 cm^{-1} are associated with ν_b and ν_a, respectively, in phosphabenzene. Their nuclear spin statistics and negative inertial defects are consistent with this. The spin statistics for ν_c and ν_d indicate antisymmetric states. The analogous low-frequency modes in pyridine of this symetry are: $\nu_{6a}(B_1)$, 605 cm^{-1}; $\nu_1(B_2)$, 675 cm^{-1} (*11*) or 749 m^{-1} (*12*); and $\nu_{11}(B_2)$, 700 cm^{-1}. It is not possible to assign ν_c and ν_d unambiguously among these alternatives. The negative inertial defects do not necessarily eliminate ν_{6a} from consideration since this state could have a negative inertial defect, especially if another out-of-plane mode is close to it (*6*).

Dipole moment. The dipole moment was determined from the Stark shift of the three transitions listed in Table IV. These data gave a dipole moment of 1.54 ± 0.02 D. Interestingly this is identical to the dipole moment reported for

TABLE IV

STARK COEFFICIENTS ($MHzV^{-2}$ cm^2) AND DIPOLE MOMENT FOR PHOSPHABENZENE

Transition	$\Delta\nu/\epsilon^2$ obsd	$\Delta\nu/\epsilon^2$ calcd
$3_{21} \rightarrow 4_{22}$ $M = 1$	-4.20×10^{-6}	-4.19×10^{-6}
$3_{22} \rightarrow 4_{23}$ $M = 1$	$+5.15 \times 10^{-6}$	5.12×10^{-6}
$4_{22} \rightarrow 5_{23}$ $M = 2$	-1.94×10^{-6}	-1.95×10^{-6}
	$\lvert\mu\rvert = 1.54 \pm 0.02$ D	

2,4,6-triphenyl phosphabenzene (*14*). The direction of the dipole moment along the symmetry axis can not be determined from these data. Oehling and Schweig using the CNDO/2 formalism, calculated the charge distribution in phosphabenzene and pyridine (*15*). They concluded that the negative end of the dipole is oriented in the same direction in both compounds, viz., towards the hetero atom.

CONCLUSION

The microwave spectrum of phosphabenzene is consistent with the interpretation that the phosphorus atom participates in π conjugation with the carbon atoms. The molecule is planar with C_{2v} symmetry. The low frequency vibrational modes, when compared with pyridine, are reasonable for a conjugated planar species. Finally, while a unambiguous value could not be determined, the limits placed on the PC bond length are indicative of some double bond character.

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