# The Nuclear Magnetic Resonance Spectra of Phosphabenzene, Arsabenzene, and Stibabenzene

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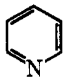
**Abstract:** The high-resolution proton and $^{13}C$ nuclear magnetic resonance spectra of phosphabenzene, arsabenzene, and stibabenzene have been measured as well as the $^{31}P$ spectrum of phosphabenzene. The proton chemical shifts and all of the proton-proton coupling constants have been determined by computer spectral simulation. The $\alpha$ protons are highly deshielded due to the diamagnetic anisotropy of the adjacent heteroatom. The phosphorus of phosphabenzene is highly deshielded. Although the $\beta$- and $\gamma$-carbon chemical shifts are in the normal aromatic region, the $\alpha$-carbon atoms occur at very low field, perhaps also due to the diamagnetic effect of the large heteroatom. All the one bond $^{13}C$ hydrogen coupling constants are close to 159 Hz.

The group 5 heteroaromatic compounds pyridine (I), phosphabenzene (II),[2] arsabenzene (III),[2] stibabenzene (IV),[3] and bismabenzene (V)[4] form a unique series in which elements of an entire column are incorporated into aromatic rings. Pyridine itself has been long known and much studied, but its heavier homologues have only recently become available.[2-4] A comparative study of the spectra and chemical properties of this series should be particularly useful in assessing theories of aromaticity. Studies of the photoelectron spectra of I, II, III, and IV,[5] microwave spectra of II[6] and III,[7] and gas phase electron diffraction of II[8] and III[8,9] have appeared. However, only preliminary reports of the NMR spectra of II,[2,10] III,[2] and IV[3] are available. The present paper summarizes our work on the $^1H$ NMR and $^{13}C$ NMR spectra of II, III, and IV as well as the $^{31}P$ NMR spectrum of II.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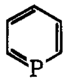
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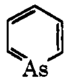
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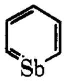
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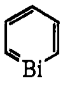
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## Proton Chemical Shifts

Proton NMR spectra of phosphabenzene, arsabenzene, and stibabenzene have been obtained in dilute chloroform solutions using a 100 MHz Varian HA-100 spectrometer. The spectrum of each of the three compounds consists of an $AB_2X_2$ pattern, in which the two $\alpha$ protons ($X_2$) lie downfield of the $\gamma$-$\beta$ ($AB_2$) multiplet. A typical spectrum, that of arsabenzene, is shown in Figure 1. Spectra of phosphabenzene were obtained with and without $^{31}P$ decoupling in order to facilitate measurement of the coupling constants. Chemical shifts and proton-proton coupling constants have been determined by spectral simulation using the LAOCN-3 program. This program was borrowed from the Quantum Chemistry Program Exchange (No. 111) and modified for use in an interactive mode on a graphics terminal of an IBM 360-67 computer at the University of Michigan. Simulated spectra were iterated to a best fit and plotted assuming a 1.0 Hz line width and Lorenzian shape. Figure 2 shows a simulated spectrum of arsabenzene. Computed proton chemical shifts and coupling constants are recorded in Tables I and II.

The most striking feature of the proton spectra is a large downfield shift of the $\alpha$ protons that increases progressively with atomic number of the group 5 atom. This shift, relative to benzene, increases from 1.24 ppm for phosphabenzene to 2.31 ppm for arsabenzene and 3.57 ppm for stibabenzene. The $\beta$ and $\gamma$ shifts also follow the same qualitative downfield trend as the $\alpha$-proton shifts, but the shift magnitudes are considerably smaller. Among these protons the largest effect is a 0.87 ppm downfield shift for $H_\beta$ in stibabenzene. Pyridine, by comparison, does not fit into the simple monotonic trend shown by the other group 5 heteroaromatics. Although $H_\alpha$ in pyridine exhibits a substantial downfield shift (1.23 ppm), $H_\beta$ and $H_\gamma$ are shifted upfield with respect to benzene and show an inverted order (i.e., $\delta^\alpha > \delta^\gamma > \delta^\beta$).

Proton chemical shifts in the heteroaromatics are most readily analyzed in terms of the changes, with respect to benzene, in shielding constant that result from substitution of the group 5 atom into the ring. Only intramolecular contributions to the shift will be considered since data for all compounds, including the benzene reference, were obtained from dilute chloroform solutions. Purely intramolecular effects on the proton shifts can be expressed as a sum of four physical interactions, which include (1) changes in diamagnetic currents in the proton s orbitals that accompany changes in s-electron density, (2) magnetic anisotropy of the group 5 atom, (3) changes in ring current, and (4) electrostatic polarization of carbon-hydrogen bonds due to neighboring bond moments.[11] Bond moments are expected to be small in the heteroaromatics considered here (excluding pyridine), and it is shown below that a consistent explanation of the major trends of proton shifts can be obtained without including through-space electrostatic effects. Of the remaining three terms, only the second (magnetic anisotropy of the group 5 atom) predicts large downfield shifts in qualitative agreement with observed shifts for $\alpha$ and $\beta$ protons.

Insertion of a group 5 atom into the ring leads to changes in s-electron density on the $\alpha$ hydrogens and is expected to produce high field shifts as the group 5 atom becomes increasingly electropositive. According to the Allred-Rochow electronegativity scale, electronegativity decreases from carbon to antimony with an inverted order for phosphorus and arsenic: C(2.60) > P(2.06) < As(2.20) > Sb(1.82).[12] CNDO/2 calculations of total electron density[13] concur with simple electronegativity predictions that $C_\alpha$ of phospha- and arsabenzene bear a net negative charge and consequently that $H_\alpha$ should experience a moderate upfield shift due to inductive effects. The approximate magnitude of this shift can be estimated from the correlation of Narasimhan and Rogers,[14] who examined the effect of substitution of various elements on the methylene proton shift of the corresponding ethyl derivatives. Using their correlation, the $\alpha$-inductive shift due to an element of electronegativity $E$ that is substituted for carbon is given by $\Delta(\delta_\alpha) = 1.61(E - E_c)$. Although this correlation is intended to apply to protons bonded to saturated carbon, we would expect it to provide at least a semiquantitative estimate of the $\sigma$-inductive effect for sp$^2$ carbon. The shifts predicted on this basis for phosphabenzene, arsabenzene, and stibabenzene are −0.78, −0.44, and −1.10 ppm, respectively. Observed shifts are in the opposite direction and are substantially larger than predicted: +1.24, +2.31, and +3.57 ppm, respectively.

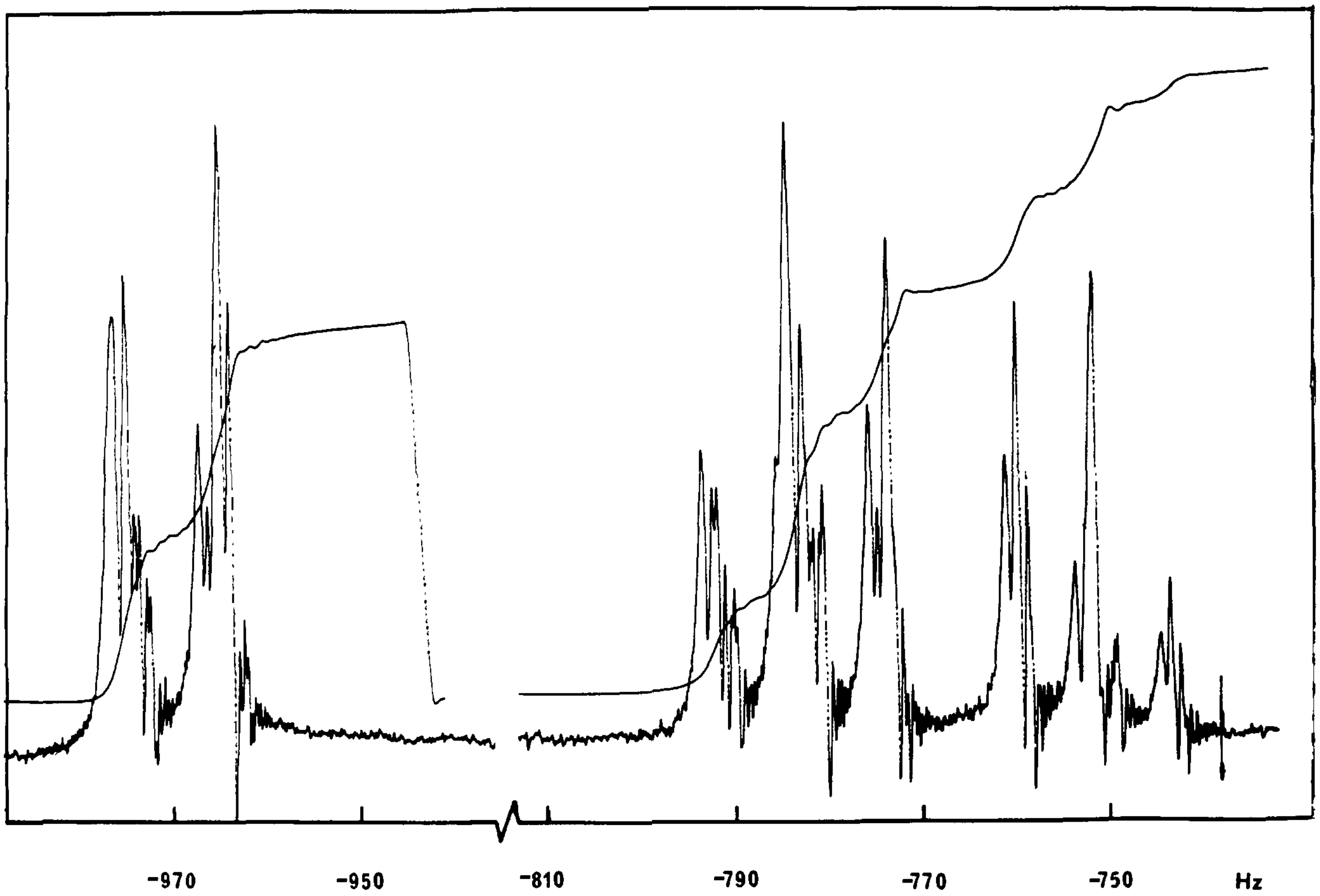

Figure 1. Proton NMR spectrum of arsabenzene.

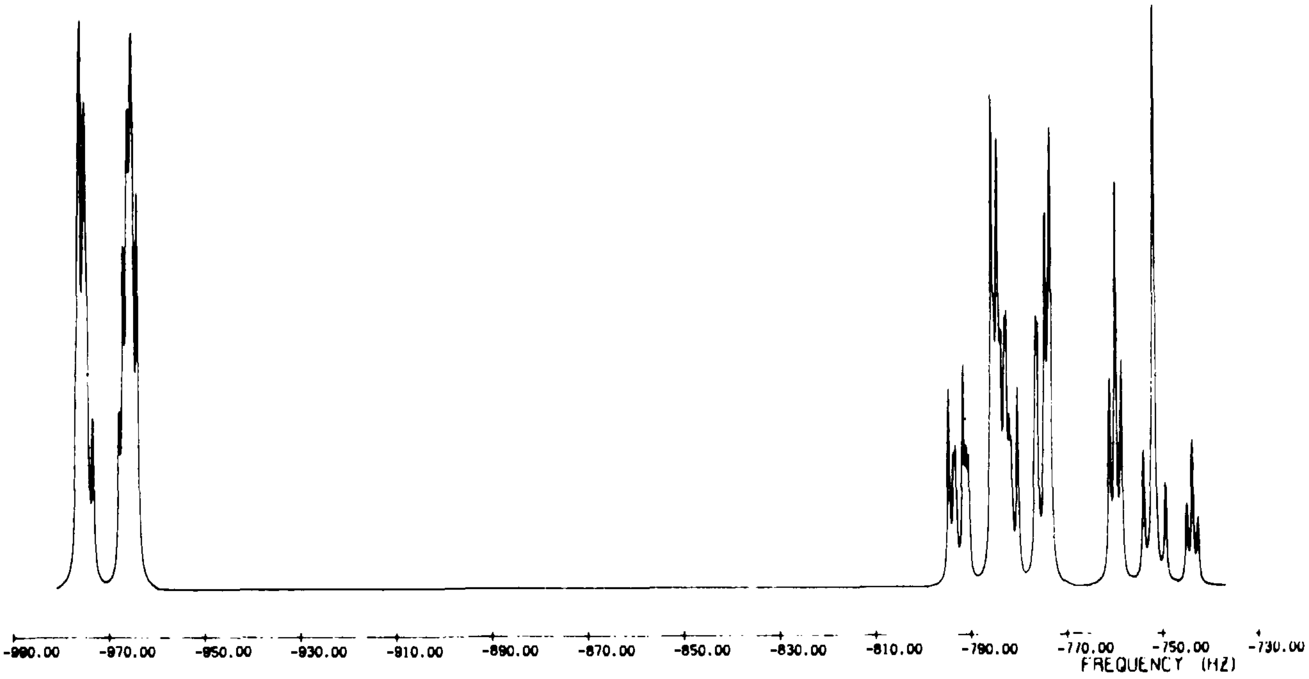

Figure 2. Computer simulated proton NMR spectrum of arsabenzene.

The large observed downfield shifts are most readily explained in terms of the magnetic anisotropy of the group 5 atom. This shift can be to either high or low field, depending on the direction of the major axis of the susceptibility tensor, and is strongly dependent on internuclear separation ($R_{AB}^{-3}$ in the dipole approximation) as is required to explain the unusually large shifts of the $\alpha$ hydrogens. Magnetic susceptibility anisotropies of the group 5 elements are also expected to increase with atomic number in qualitative agreement with the trend in observed chemical shifts.[15]

The dipolar portion of the magnetic anisotropy contribution to the shift has been derived by McConnell:[16]

$$\Delta\sigma_m = (3N_0R_{AB})^{-3}[2\Delta\chi_1 - \Delta\chi_1 3\cos^2\theta_Z - \Delta\chi_2] \quad (1)$$

$$\Delta\chi_1 = \chi_{zz} - \chi_{yy},\ \Delta\chi_2 = \chi_{zz} - \chi_{xx}$$

The $x$ axis is taken to be perpendicular to the molecular plane

Table I. The Proton Chemical Shifts of the Heterobenzenes[a]

| Position | Benzene | Pyridine[b] | Phosphabenzene | Arsabenzene | Stibabenzene |
|---|---|---|---|---|---|
| $H_\alpha(H_2,H_6)$ | 7.37 | 8.29 | 8.61 | 9.68 | 10.94 |
| $H_\beta(H_3,H_5)$ | | 7.38 | 7.72 | 7.83 | 8.24 |
| $H_\gamma(H_4)$ | | 7.75 | 7.38 | 7.52 | 7.78 |

[a] Chemical shift values are in ppm downfield from TMS. [b] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

Table II. Proton-Proton Coupling Constants of the Heterobenzenes

| | Pyridine[a] | Phosphabenzene | Arsabenzene | Stibabenzene[b] |
|---|---|---|---|---|
| $J_{23}$ | 5.5 | 10.0 | 10.0 | 12.5 |
| $J_{24}$ | 1.9 | 1.2 | 1.0 | |
| $J_{25}$ | 0.9 | 1.2 | 1.5 | |
| $J_{26}$ | 0.4 | −1.9 | −0.4 | |
| $J_{34}$ | 7.5 | 9.1 | 8.1 | 9.0 |
| $J_{35}$ | 1.6 | 1.8 | 2.5 | |

[a] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, **35**, 1487 (1957). [b] The quality of the spectrum of stibabenzene was considerably poorer than for the other heterobenzenes.

and $y$ is taken as the twofold axis. In principle, the two anisotropies can be determined from the $\alpha$, $\beta$, and $\gamma$ shifts. In practice this solution is not very satisfactory because the $\beta$ and $\gamma$ shifts are much smaller than the $\alpha$ shift and may not be as strongly dominated by magnetic anisotropy. A satisfactory description of the shifts can be obtained, however, if the main currents are assumed to be coaxial with the $p_z$ orbital of the group 5 atom. Then the principal axis of the shielding cone is perpendicular to the ring, $\Delta\chi_1 = \Delta\chi_2$, and all the protons lie in the plane of maximal deshielding. Equation 1 then reduces to $\Delta\sigma = (\chi_\parallel - \chi_\perp)/3N_0R_{AB}{}^3$. For this orientation, all proton shifts in a given compound are linear in $R_{AB}{}^{-3}$ with a slope equal to $(\chi_\parallel - \chi_\perp)/3N_0$ and an intercept equal to the benzene shift. These plots are shown in Figure 3. Chemical shifts of the $\alpha$ protons have been corrected for inductive effects using the correlation of Narasimhan and Rogers. The plots are reasonably linear, which supports the choice of orientation of the shielding cone assumed above. The intercepts are to high field of the benzene chemical shift for all three molecules and increase regularly from phosphabenzene ($\delta_0 = -0.37$ ppm) to stibabenzene ($\delta_0 = -0.80$ ppm). This residual upfield shift that remains when magnetic anisotropy effects are extrapolated to zero is consistent with decreasing ring currents in the heteroaromatics. Ring currents produce essentially the same induced field at all protons in the ring and will affect the intercepts but not the slopes of the straight lines.

The extent of aromaticity has frequently been estimated from the magnitude of the induced diamagnetic ring current.[17] It has been argued that the regular increase in chemical reactivity of the group 5 heteroaromatics with increasing atomic number of the heteroatom implies a regular decrease in their delocalization energy and hence aromaticity.[4] Thus it is reassuring that the decreasing ring current of the heavier heteroaromatics reinforces these chemical arguments.

Magnetic anisotropies have been computed from the slopes of the plots in Figure 3 and are found to be: $\Delta\chi_P = 62 \times 10^{-6}$, $\Delta\chi_{As} = 103 \times 10^{-6}$, and $\Delta\chi_{Sb} = 202 \times 10^{-6}$. These values are quite large in comparison to the anisotropies of typical nonaromatic organic compounds ($\Delta\chi \sim 2\text{-}20 \times 10^{-6}$)[18] and the values obtained for arsenic and antimony are even large compared to the anisotropy associated with aromaticity, e.g.,

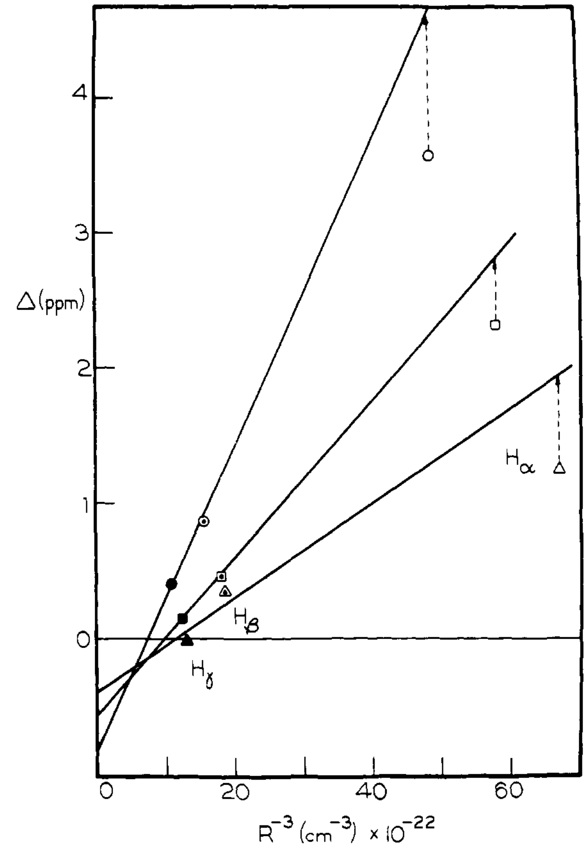

**Figure 3.** Proton chemical shifts of phosphabenzene (▽), arsabenzene (⊡), and stibabenzene (⊙) vs. $R^{-3}$, where $R$ is the internuclear distance between the group 5 atom and $H_\alpha$, $H_\beta$, or $H_\gamma$. Dashed lines indicate the magnitude of $\sigma$-inductive effects. Internuclear distances for arsabenzene and phosphabenzene were calculated from electron diffraction data;[8,9] $R^{-3}$ for stibabenzene is based on the assumed bond lengths $\gamma_{CC} = 1.395$ Å and $\gamma_{C\text{-}Sb} = 2.05$ Å and CSbC bond angle of 94°. Positive shifts are to low field and are referenced to benzene in dilute chloroform solution ($\delta$ 7.37).

$\Delta\chi = 60 \times 10^{-6}$ for benzene.[19] If the observed downfield shifts are attributed to magnetic anisotropy, however, $\Delta\chi$ will necessarily be quite large because of the large internuclear distance[8,9] and the fact that the shift varies as $R^{-3}$. Repositioning the magnetic dipole along the C-X bond would not give smaller values of $\Delta\chi$ since this would require that the major tensor axis simultaneously be tilted toward the bond axis, thus bringing the $\alpha$ protons closer to the shielding cone. Whether the magnetic anisotropy is as large as the proton shifts appear to indicate could be determined directly by observing the second-order Zeeman effect in microwave spectra in the manner of Flygare and co-workers.[18]

**$^{31}$P NMR Spectrum.** The $^{31}$P NMR spectrum of phosphabenzene is illustrated in Figure 4. The phosphorus chemical shift value is 211 ppm downfield from 85% $H_3PO_4$, while the phosphorus-proton coupling constants are: $^2J_{P\text{-}H_2} = 38$ Hz, $^3J_{P\text{-}H_3} = 8$ Hz, and $^4J_{P\text{-}H_4} = 3.5$ Hz. The deshielding is very great in comparison with most three-coordinate phosphorus compounds. The spectra of several derivatives of phosphabenzene have been reported. All exhibit signals in the range 178.2 to 209, which appears characteristic for phosphabenzene.[20]

**$^{13}$C Chemical Shifts.** The $\delta$ $^{13}$C of phosphabenzene, arsabenzene, and stibabenzene are shown in Table III. The spectra were obtained in $CDCl_3$ solutions at 25.16 MHz in the FT mode on a JEOL JNM-PFT/100 NMR spectrometer using random noise proton decoupling. Assignment of the signals for the $\gamma$ carbons was made on the basis of their lower intensities. In order to distinguish between the $\alpha$ and $\beta$ carbons of phos-

**Table III.** $^{13}C$ Chemical Shifts of the Heterobenzenes and 2-Methyl Heterobenzenes

| | Benzene[a] | Toluene[a,b] | Pyridine[a] | 2-Methylpyridine[a] | Phosphabenzene | 2-Methylphosphabenzene | Arsabenzene | 2-Methylarsabenzene[d] | Stibabenzene[e] |
|---|---|---|---|---|---|---|---|---|---|
| $\delta$ $C_2$ | 128.7 | 137.8 | 150.6 | 159.9 | 154.1 | 166.9 | 167.7 | 182.9 | 178.3 |
| $\delta$ $C_3$ | | 129.3 | 124.5 | 123.4 | 133.6 | 130.7[c] | 133.2 | 131.0[c] | 134.4 |
| $\delta$ $C_4$ | | 128.5 | 136.4 | 137.2 | 128.8 | 128.7 | 128.2 | 129.2 | 127.4 |
| $\delta$ $C_5$ | | 125.6 | | 122.0 | | 134.1[c] | | 134.4[c] | |
| $\delta$ $C_6$ | | 129.3 | | 149.8 | | 153.9 | | 168.3 | |
| $\delta$ $C_7$ | | 21.3 | | 25.8 | | 24.7 | | 26.0 | |

[a] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972. [b] For consistency in this table the carbon atom bearing the methyl group is numbered 2. [c] The relative assignment for $\delta$ $C_3$ and $\delta$ $C_5$ is uncertain. [d] Solvent contained 30% tetrahydrofuran. [e] The solvent contained 10% diglyme and the spectrum was recorded at −10 °C. All other spectra were recorded at ambient temperature.

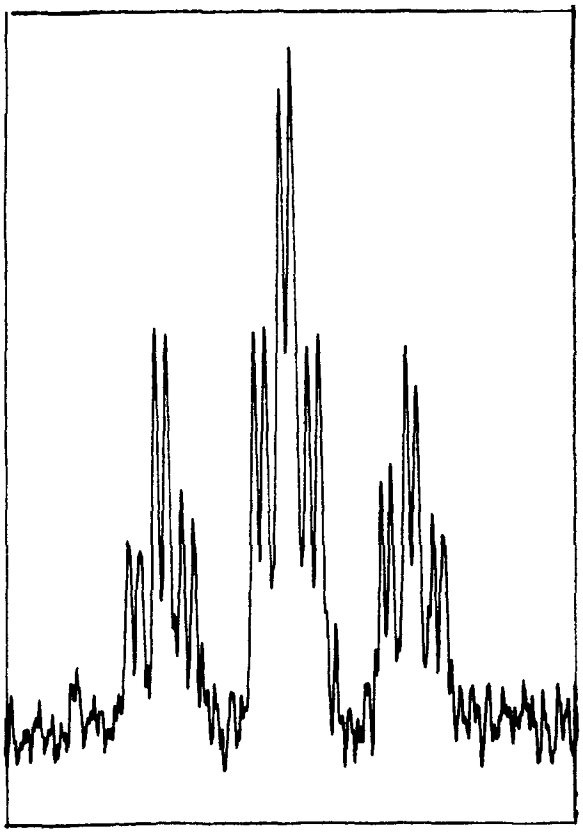

**Figure 4.** $^{31}P$ nuclear magnetic resonance spectrum of phosphabenzene.

phabenzene and arsabenzene, the spectra of the available 2-methyl derivatives[21] were examined. The methyl substituent effects are very similar to those found in toluene and $\alpha$-picoline, although the 2 position is somewhat more deshielded by the methyl group. For stibabenzene the lowest field signal was assigned to the $\alpha$ carbon in analogy to its homologues.

The relative order of the carbon chemical shifts of phosphabenzene, arsabenzene, and stibabenzene is the same as that observed for the corresponding protons in $^1H$ NMR spectra. That is, the $\alpha$ carbons are considerably deshielded relative to benzene, while the $\beta$ carbons are somewhat deshielded and $\gamma$ carbons have almost the same chemical shift as benzene. This ordering contrasts with that of the pyridine, in which the $\alpha$ and to a smaller extent the $\gamma$ carbon are deshielded, while the $\beta$ carbons are shielded. Again the ordering in pyridine is the same as is observed for the protons attached to the corresponding carbon atoms.

There is rather little variation in $\beta$ and $\gamma$ carbons of phosphabenzene, arsabenzene, and stibabenzene. However, the deshielding of the $\alpha$ carbons is progressive in the series pyridine, phosphabenzene, arsabenzene, and stibabenzene. For stibabenzene this amounts to nearly 50 ppm relative to benzene. Again this reflects a similar trend in $\alpha$ protons of these compounds.

This extreme shift to lower field is the most striking feature of the spectra. On a qualitative basis the ordering of chemical shifts of pyridine is easily appreciated. A variety of MO calculations[13,22,25] indicates, and chemical experience suggests, that the $\alpha$ and to a smaller extent the $\gamma$ carbons of pyridine bear a degree of positive charge while the $\beta$ carbons bear a net negative charge. Generally, the azines show a good proportionality between $\delta_c$ and MO-predicted total electron densities.[23,24] The shifts are downfield with increasing negative charge with a slope of 160 ppm/electron.

On the other hand charge density effects cannot be responsible for the extreme deshielding of phosphabenzene, arsabenzene, and stibabenzene. Such an explanation would require the $\alpha$-carbon atoms to become increasingly positive as the heteroatom becomes increasingly electropositive. Obviously it would be more reasonable to expect the reverse effect and indeed MO calculations on phosphabenzene and arsabenzene do predict that the $\alpha$ carbons are net electron acceptors.[13,25] CNDO/2 calculations indicate that phospha- and arsabenzene gain 0.134 and 0.144 units of negative charge, respectively, at the $\alpha$ carbon,[13] which should result in *upfield* shifts of 21.4 and 23.0 ppm relative to benzene according to the correlation of Spiesecke and Schneider.[23] The observed shifts are *downfield* by 16.3 and 39.0 ppm.

The source of these large $\alpha$-carbon downfield shifts can be sought in Karplus and Pople's molecular orbital theory of magnetic shielding.[26] They have expressed the total shielding constant $\sigma_A$ of atom A as a sum of terms

$$\sigma_A = \sigma_A{}^d + \sigma_A{}^p + \sum_{B \neq A} \sigma_{AB} + \sigma_R \qquad (2)$$

due respectively to diamagnetic currents on atom A, paramagnetic currents on atom A, diamagnetic and paramagnetic currents on other atoms B, and ring currents. Of these four terms, the paramagnetic term, $\sigma_A{}^p$, usually exhibits much larger variations with changes in chemical environment than do the others and is responsible for major trends of observed carbon shifts. Numerical calculations of Tokuhiro and Fraenkel[24] indicate that the charge dependence of $\sigma_p{}^A$ accounts almost entirely for the observed chemical shifts in the azines. About half of the dependence (85 ppm/electron) results from contraction of the 2p orbitals upon withdrawal of electronic charge. A similar shift (73 ppm/electron) results from the dependence of the average excitation energy and elements of the bond order matrix upon charge density. Thus the $\alpha$-carbon shifts of phospha-, arsa-, and stibabenzene, which vary in the opposite manner, appear to arise from a different term in eq 2. Tokuhiro and Fraenkel have also calculated $\Delta\sigma_A{}^d$ in the azines and found that it contributes very little, generally less than 1 ppm, to the shift. Variations in ring currents are far too small and are in the wrong direction to account for shifts of the

**Table IV.** The $^{1}J_{^{13}\mathrm{CH}}(\mathrm{H}_2)$ of the Heterobenzenes with the Interior Bond Angles

| Position | Benzene[d] | Pyridine[d] | Phosphabenzene | Arsabenzene |
|---|---|---|---|---|
| $C_2$ | 159<br>(120°) | 180<br>(123.8°)[a] | 157<br>(124.4°)[b] | 159<br>(125.1°)[b,c] |
| $C_3$ | | 160<br>(118.5°)[a] | 156<br>(123.6°)[b] | 157<br>(124.1°)[b,c] |
| $C_4$ | | 157<br>(118.4°)[a] | 161<br>(122.8°)[b] | 161<br>(124.2°)[b,c] |

[a] G. O. Sorensen, L. Mahler, and N. Rastrup-Andersen, *J. Mol. Struct.*, **20**, 119 (1974). [b] T. C. Wong, Ph.D. Thesis, The University of Michigan, 1974. [c] T. C. Wong, A. J. Ashe, III, and L. S. Bartell, *J. Mol. Struct.*, **25**, 65 (1975). [d] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

**Table V.** $J_{^{31}\mathrm{P}-^{13}\mathrm{C}}(\mathrm{H}_2)$ of Phosphabenzene and 2-Methylphosphabenzene

| | Phosphabenzene | 2-Methylphosphabenzene |
|---|---|---|
| $C_2$ | 53 | 53 |
| $C_3$ | 14 | 14[a] |
| $C_4$ | 22 | 18 |
| $C_5$ | | 16[a] |
| $C_6$ | | 51 |
| $C_7$ | | 37 |

[a] The relative assignment of $C_3$ and $C_5$ is uncertain.

observed magnitudes.[27] Thus the most likely source of the extreme $\alpha$-carbon deshielding are the interatomic terms, $\Sigma_{\mathrm{B}}\sigma_{\mathrm{AB}}$, and in particular that term associated with currents centered on the group 5 atom. Diamagnetic currents centered on the group 5 atom almost certainly cause the downfield shifts observed in the proton spectra and provide a natural explanation for the qualitatively similar trends of the $\alpha$-carbon and $\alpha$-proton chemical shifts. The magnitude of the effect in the carbon spectra is much too large to be described by the simple dipolar picture of anisotropic magnetic susceptibility, however. Assuming that relative shifts vary as $R_{\mathrm{AX}}^{-3}$ and using the susceptibility components derived from the proton spectra, carbon chemical shifts (referenced to benzene) of 6.6, 9.1, and 14.3 ppm are predicted for phospha-, arsa-, and stibabenzene, as compared to measured values of 25.4, 39.0, and 49.6 ppm. If currents arising in the group 5 atom are indeed the dominant shift mechanism, certainly McConnell's theory, which assumes that the orbitals giving rise to the diamagnetic currents are highly localized on atoms distant from A, is quantitatively inadequate. The $\alpha$-carbon shifts are probably sensitive to delocalization of the large electron densities from the group 5 atoms onto the $\alpha$ carbons, and it is quite possible that Pople's description of neighboring atom effects as a sum of atomic contributions [as implied by eq 2] is inappropriate.

In this regard it is interesting to compare the $\alpha$-carbon shifts to those of the five-membered ring heterocycles, thiophene, selenophene, and tellurophene. Large progressive downfield shifts at the $\alpha$ carbons are not observed in these compounds whereas the $\alpha$ protons are strongly deshielded,[28] presumably due to magnetic anisotropy. This difference between the six-membered ring group 5 heteroaromatics and the five-membered group 6 may come from differences in the degree of electron delocalization between the two classes of compounds. A detailed theoretical investigation of the $\alpha$-carbon shift should prove interesting.

**$^{13}$C–H and $^{13}$C–$^{31}$P Constants.** In order to obtain $J_{\mathrm{CH}}$ values for phosphabenzene and arsabenzene proton coupled spectra were recorded. The lower stability of stibabenzene has frustrated attempts to obtain $J_{\mathrm{CH}}$'s from its dilute solutions. In addition to the large one-bond $^{13}$CH coupling the $\alpha$- and $\gamma$-carbon signals occur at 8-Hz triplets, while the signal for the $\beta$ carbon is an 8-Hz doublet. Coupling smaller than 1 Hz was not resolved. This indicates that the $^{3}J_{\mathrm{CH}}$ values are larger than those for $^{2}J_{\mathrm{CH}}$ as is the case in other aromatic compounds.[29]

The one-bond $^{13}$CH coupling constants for phosphabenzene and arsabenzene together with those for pyridine and benzene are listed in Table IV. Certainly the most striking feature of these parameters is the near identity of all the coupling constants save that of the $\alpha$ carbon of pyridine.

Carbon-proton coupling constants are usually dominated by the Fermi contact term and are therefore related to the percent s character of the C–H bond as well as to the effective nuclear charge of carbon.[30] The known interior bond angles of the heavier heterobenzenes (shown in parentheses in Table IV) only slightly exceed the 120° expected for pure sp$^2$ hybridization.[8,9] The external C–H bonds must have a hybridization close to sp$^2$ and $^{1}J_{\mathrm{CH}}$ values close to that of benzene are expected.

On the other hand, the $^{1}J_{\mathrm{CH}}$ of the $\alpha$-carbon atoms of pyridine is considerably larger than the others. In general the introduction of atoms more electronegative than carbon in a molecule has the effect of increasing $^{1}J_{\mathrm{CH}}$ at the adjacent carbon atom. This effect is well documented for the nitrogen heteroaromatics.[32] One may rationalize the effect by assuming that the electronegative atom withdraws electron density predominantly from the higher energy carbon p orbital, increasing the s character of the C–H bond. Conversely, the introduction of a relatively electropositive element might be expected to decrease the CH coupling constant below the value expected for benzene. Obviously the data in Table IV do not support this expectation. However, the theoretical relation between coupling constants and molecular bonding is a complex one[11,30] and the failure of this simple correlation is not particularly surprising.

Carbon-phosphorus coupling constants were measured from the $^{13}$C-NMR spectra and are listed in Table V. The coupling constants follow the trend $^{1}J_{\mathrm{CP}} > {}^{2}J_{\mathrm{CP}} < {}^{3}J_{\mathrm{CP}}$ that has been previously found for substituted phosphabenzenes.[10] A qualitatively similar trend, in which the two-bond coupling constant is smaller than the three-bond coupling constant, has also been reported in $^{15}N$-pyridine.[33]

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# Internal Rotation in Some Oxalyl Halides. A Theoretical Investigation

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**Abstract:** Ab initio molecular orbital theory is used to study internal rotation in oxalyl fluoride, oxalyl chlorofluoride, and oxalyl chloride. The theoretical results indicate the presence of both trans and cis conformations for oxalyl fluoride and oxalyl chlorofluoride with the trans conformation being somewhat more stable than the cis. Oxalyl chloride on the other hand is predicted to have trans and gauche conformations with no stable cis conformation and with the trans conformation being the more stable. These results are compared with those derived from spectroscopic studies. An examination of the factors determining the shape of the energy curves is given.

Extensive use has been made of molecular orbital theory in recent years to study the change in the energy of molecules with internal rotation about single bonds.[1-3] Pople and his co-workers[4] have investigated the internal rotation about the carbon-carbon bond in glyoxal (CHO-CHO) and have predicted the existence of both a trans and a cis conformation with the former being more stable by 6.1 kcal/mol, in close agreement with another theoretical study of Pincelli, Cadioli, and David[5] who obtained a separation of 6.4 kcal/mol for the two conformations, and it is to be compared with an experimental value of 3.2 kcal/mol.[6] However, except for a somewhat limited theoretical treatment of oxalyl chlorofluoride using the CNDO/2 method by Pople and Segal,[7] no theoretical calculations have been published on the halogen derivatives of glyoxal and in particular on oxalyl chloride, oxalyl chlorofluoride, and oxalyl fluoride.

Experimental investigations of internal rotation in the oxalyl halides have been the subject of a large number of publications by many workers with significantly different interpretations of the data occurring, resulting in considerable controversy. Most of the publications have dealt with oxalyl chloride, beginning with the observation of its Raman spectrum in the liquid state by Kohlrausch and Wittek.[8] These authors made no assignments for the observed spectrum. Ziomek et al.[9] first reported the infrared spectrum of the liquid state and though no assignments were made they concluded from the fact that only two coincidences were observed between infrared and Raman frequencies that only the trans isomer was present. Saksena and Kagarise[10] obtained an infrared and Raman spectrum of the liquid and an infrared spectrum of the vapor and studied the intensity variation of the observed bands. Their conclusion was that more than one conformation was present in both liquid and vapor states and that the conformations were the trans and cis forms with the trans being more stable by 2.8 kcal/mol. There then followed a set of three more publications by Ziomek et al.,[11] by Saksena et al.,[12] and by Kagarise[13] attempting to support their respective interpretations. An x-ray analysis of solid oxalyl chloride was published by Groth and Hassel[14] indicating the presence of only a trans conformation. Hencher and King[15] analyzed the infrared and Raman spectrum of the liquid and vapor and concluded that only the trans conformation existed and Balfour and King[16] interpreted the uv spectrum in terms of only the trans conformation. Hjoortas[17] published a short note on the electron diffraction spectrum, whose analysis indicated only the presence of a trans conformation in the vapor phase. Fleury et al.[18-20] published a series of papers which concluded that oxalyl chloride exists as a cis-trans mixture with an energy difference of around 2 kcal/mol, the trans conformation being the more stable. Durig and Hannum[21] studied the infrared spectrum of the solid, liquid, and gas and the Raman spectrum of the solid and liquid and concluded that only the trans conformation was present in the solid while both cis and trans were present in the liquid and gas with the trans conformation being more stable by 2.2 kcal/mol. From the torsional vibration at 55 cm$^{-1}$ they obtain a value of $V^*$ ($= V_1 + 4V_2 + 9V_3$) equal to 11.1 kcal/mol. Finally Hagen and Hedberg[22] analyzed the electron diffraction data for the gaseous oxalyl chloride and concluded that there were two conformations but that these were the trans and the gauche with the trans being more stable by 1.38 kcal/mol and the barrier to rotation being 2.00 kcal/mol. In summary the experimental data, particularly the more recent work, supports the existence of two conformers but there is still uncertainty as to whether the less stable conformer is the cis or the gauche.

The experimental data on oxalyl fluoride have also been subject to different interpretations though there have been fewer papers published on this molecule. The infrared spectrum