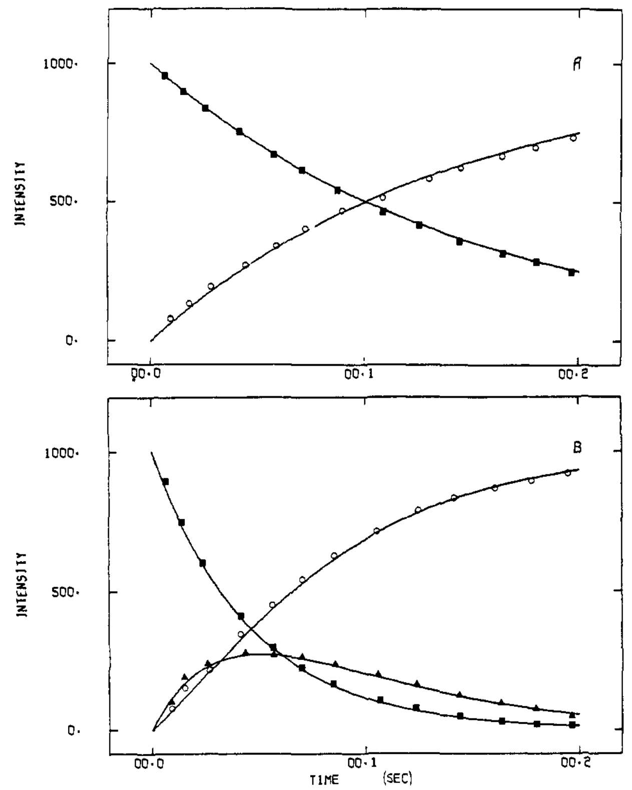

Figure 1. Proton transfer from toluene to the allyl anion. Ion intensities *vs.* time: $C_6H_5CH_2^-$ (○), $C_3H_5^-$ (■), CH_3O^- (▲). (A) Uncatalyzed reaction, pressure in 10^{-6} Torr: propene 7.0, toluene 3.0. (B) Catalyzed reaction, pressure in 10^{-6} Torr: propene 5.1, toluene 3.0, methanol 1.9. Curves were calculated from rate constants given in the text.

The observation of small rate constants and a catalytic pathway for proton transfer for these compounds in the gas phase is significant in terms of their solution chemistry. Alcohols have previously been shown to catalyze similar proton-transfer reactions in solution.[8,9] Ritchie's studies[10] have indicated that isolated molecule properties, as well as solvent reorganization, may be responsible for the well-known low "kinetic acidity" of certain carbon acids.[11] Our work constitutes a direct demonstration that intrinsic, isolated molecule and ion properties are definitely involved.

The apparent barriers in these reactions may be associated with some unique features of delocalized carbanion systems. To the extent that two of the electrons in π system become localized in the developing C-H bond as the protonation transition state is reached, delocalization must be reduced; the loss of this delocalization may be responsible for the observed barriers. This effect is not observed when protonation occurs at oxygen or nitrogen. We suggest that this is because the lone-pair electrons on these atoms allow protonation to occur orthogonal to the π system, obviating loss of delocalization. This is also in accord with the inability to observe hydrogen bonding to delocalized carbanions, the putative hydrogen bonded species having great similarities to the transition state for proton transfer. Consistent with this picture, we find that the barriers are not associated with carbanions, *per se*, since acetylide ions appear to behave normally in the gas phase.[8a,12,13c]

Recent studies have indicated that gas-phase ion chemistry can be used to help in understanding solution thermodynamic properties.[13–16] It is now apparent that in some cases insight can be gained into transition state properties as well. Work is currently underway to elucidate the nature of the activation barrier.

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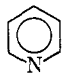
Photoelectron Spectra of Phosphabenzene, Arsabenzene, and Stibabenzene[1]

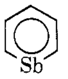
Sir:

In Figure 1 are shown the photoelectron (pe) spectra of pyridine (I), phosphabenzene[2] (II), arsabenzene[2] (III), and stibabenzene[3] (IV). The (vertical) ionization


I


II


III


IV

potentials $I_{v,J}$, *i.e.* the values corresponding to the positions of the band maxima, and a tentative assignment are given in Table I and in the correlation diagram of Figure 2.

The orbital sequence for I has been deduced previously from its photoelectron spectrum[4] and con-

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Table I. Tentative Assignment of the Bands in the Photoelectron Spectra of I, II, III, and IV[a]

	I		II		III		IV	
Band (J)	Orbital	I_v, eV	Orbital	I_v, eV	Orbital	I_v, eV	Orbital	I_v, eV
1	$11a_1(\sigma,n)$	9.7	$3b_1(\pi)$	9.2	$5b_1(\pi)$	8.8	$7b_1(\pi)$	8.3
2	$1a_2(\pi)$	9.8	$1a_2(\pi)$	9.8	$2a_2(\pi)$	9.6	$3a_2(\pi)$	9.4
3	$2b_1(\pi)$	10.5	$13a_1(\sigma,n)$	10.0	$17a_1(\sigma,n)$	9.9	$21a_1(\sigma,n)$	9.6
4	$7b_2(\sigma)$	12.5	$8b_2(\sigma)$	11.5	$10b_2(\sigma)$	11.0	$12b_2(\sigma)$	10.4
5	$1b_1(\pi)$	12.6	$2b_1(\pi)$	12.1	$4b_1(\pi)$	11.8	$6b_1(\pi)$	11.7

[a] The relative sequence of the bracketed pair of orbitals is uncertain.

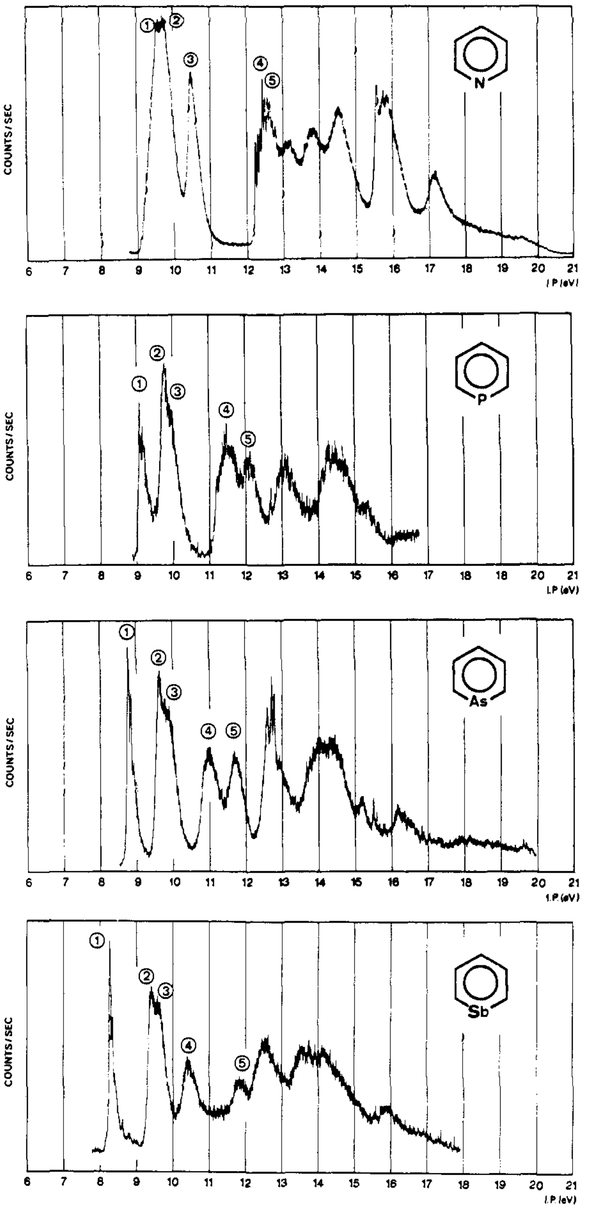

Figure 1. Photoelectron spectra of pyridine, phosphabenzene, arsabenzene, and stibabenzene.

firmed by correlation with that of substituted pyridines[5] or other aza aromatic compounds.[6]

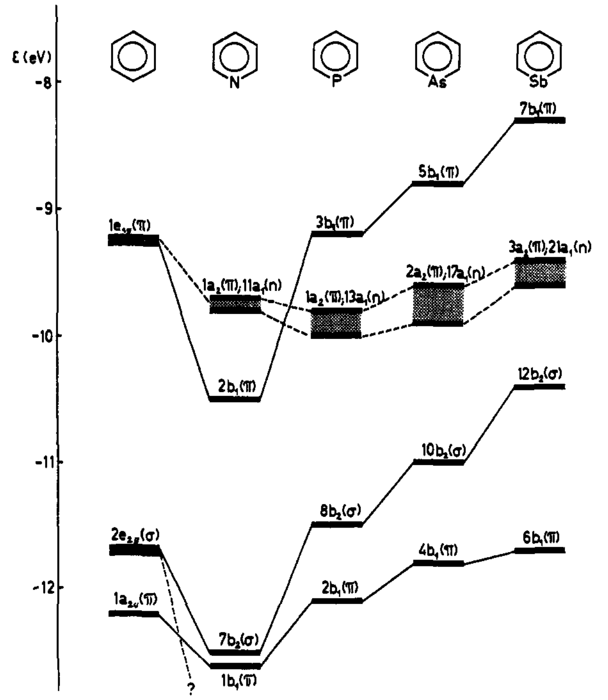

Figure 2. Orbital correlation diagram.

To aid in the assignment we have carried out *ab initio* calculations for II using an STO-3G basis set[7] and the following idealized structure parameters (*cf.* ref 8): C_{2v} symmetry, $R(\mathrm{PC}) = 1.74$ Å, $R(\mathrm{CC}) = 1.40$ Å, $\theta(\mathrm{CPC}) = 103°$, $\theta(\mathrm{PCC}) = 123°$, $\theta(\mathrm{C_2C_3C_4}) = 124°$, $\theta(\mathrm{C_3C_4C_5}) = 123°$. (These values differ insignificantly from those recently obtained by microwave spectroscopy.[9])

Standard molecular exponents[7] have been used for the s,p basis set and a d orbital exponent of 1.4. For none of the occupied orbitals is there significant d orbital contribution and the evidence from these calculations is that d orbital participation on phosphorus is unimportant in understanding structure and bonding in phosphabenzene. This conclusion has been reached by considering the lowering of the total energy of II on addition of 3d orbitals on phosphorus to the basis set, the 3d orbital population analysis, and the orbital energies and sequences with and without 3d orbitals on phosphorus. It is noteworthy that calculations on I, II, and III reproduce the inversion of $a_2(\pi)$ and $b_1(\pi)$ going from pyridine to phosphabenzene and arsabenzene. Full details of these calculations and those cur-

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rently in progress on arsabenzene will be published in due course.

Table II. *Ab Initio* Results for the Six Highest Molecular Orbitals of Phosphabenzene

Orbital	Orbital energy ϵ_J, eV
$3b_1(\pi)$	-6.16
$1a_2(\pi)$	-7.72
$13a_1(\sigma)$	-8.03
$8b_2(\sigma)$	-10.63
$2b_1(\pi)$	-11.52
$12a_1(\sigma)$	-12.79

The *ab iuitio* results for the six highest occupied molecular orbitals are shown in Table II. The corresponding ionization potentials $I_{v,J} = -\epsilon_J$, obtained by applying Koopmans' theorem, are too small compared to the observed values (*cf.* Table I, column II), but the relative sequence of the orbitals is in agreement with that deduced by correlating the spectra of I to IV.

We first show that the highest occupied molecular orbitals of II, III, and IV correspond to $2b_1(\pi)$ of I. To this end we correlate the ionization potentials $I_{v,3}$ of I and $I_{v,1}$ of II, III, and IV with the ionization potentials I(X) of the free atoms X = N, P, As, Sb ($^4S_{3/2} \rightarrow {}^3P_0$: N, 14.53 eV; P, 11.0 eV; As, 9.81 eV; Sb, 8.64 eV)[10] as independent variables. A linear least-squares fit yields

$$I_v(b_1(\pi)) = 5.24 \text{ eV} + 0.362I(\text{X}) \qquad (1)$$

$$r = 0.9998$$

As indicated by the correlation coefficient the regression is almost perfect. Note that for $I(\text{C}) = 11.26$ eV we obtain from eq 1 $I_v(b_1(\pi)) = 9.32$ eV, to be compared with $I_{v,1} = 9.24$ eV, the first ionization potential of benzene (ejection from $e_{1g}(\pi)$).[11] The benzene orbital corresponding to $b_1(\pi)$ in I–IV has an atomic orbital coefficient of $1/(3)^{1/2}$ in position 1. Consequently, a first-order perturbation treatment leads us to expect a slope of $(1/(3)^{1/2})^2 = 1/3$ for regression 1, a value in excellent agreement with the one obtained.

If we assume that the same type of correlation procedure can be applied to the second $b_1(\pi)$ orbitals of I–IV, then we would expect a regression line with slope $(1/(6)^{1/2})^2 = 1/6$ passing through the points $I_v(1b_1(\pi)) = 12.6$ eV and $I(\text{N}) = 14.53$ eV for I, and $I_v(2b_1(\pi)) = 12.1$ eV and $I(\text{P}) = 11.0$ eV for II. Indeed, the linear regression based on the ionization potentials $I_{v,J}$ assigned to the second $b_1(\pi)$ orbitals in Table I yields

$$I_v(b_1(\pi)) = 10.25 \text{ eV} + 0.163I(\text{X}) \qquad (2)$$

$$r = 0.9908$$

The slope is exactly as predicted and for $I(\text{C}) = 11.26$ eV we find $I_v(b_1(\pi)) = 12.09$ eV to be compared to $I(a_{2u}(\pi)) = 12.2$ eV for benzene.

The fact that plotting the experimentally observed ionization potentials of the two $b_1(\pi)$ orbitals *vs.* the corresponding ionization potentials of the free atoms X = N, P, As, and Sb yields strictly linear relationships 1 and 2 with slopes that agree with those derived from HMO models by first-order perturbation arguments may seem surprising. However, it can be shown that changes in the coulombic term α in position 1 by $\delta\alpha_X$ in the range $-3 \text{ eV} < \delta\alpha_X < +3$ eV will yield second-order corrections, *i.e.* deviations from the first-order straight line which are smaller than $\sim$0.2 eV even for the extreme values of $\delta\alpha_X$.

Little change in orbital energy is expected for the $a_2(\pi)$ orbital as we go from I to IV as this orbital has a node passing through atoms 1 and 4.

The inversion of ordering of the $b_1(\pi)$ and $a_2(\pi)$ orbitals in going from I to II is readily understandable on the basis of the electron distribution in the two molecules. Previous *ab initio* calculations have shown that in I the nitrogen atom is overall an electron acceptor and hence stabilizes the $b_1(\pi)$ component of the benzene $e_{1g}(\pi)$ level with respect to the $a_2(\pi)$. For II the reverse obtains since our calculations show that phosphorus is overall electron releasing.

The pe spectroscopic investigation of ammonia, phosphine, arsine, and stibine[12] has shown that the lone-pair orbitals of P, As, and Sb are essentially of s character and that their orbital energies are close to the lone-pair orbital energy of ammonia: NH_3, 10.9 eV; PH_3, 10.6 eV; AsH_3, 10.5 eV; SbH_3, 10.0 eV. We believe that the intense double bands in the region 9.5–10 eV are due in each case to two overlapping bands corresponding to ejection from $a_2(\pi)$ and $a_1(\sigma,n)$ (relative order uncertain).

It could be argued that in the spectrum of II and III the second band is more vertical than the third, implying that in these two compounds $a_2(\pi)$ is above $a_1(\sigma,n)$. However, such an assignment should be taken with a grain of salt and only be used as a working hypothesis.

The tentative assignment so obtained is summarized in the correlation diagram of Figure 2. As far as the upper three orbitals of II are concerned, the assignment is compatible with the one proposed previously for 2,4,6-tri-*tert*-butylphosphabenzene.[13]

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