at 335 nm (ϵ 1.19 × 10^4 M^{-1} cm^{-1}) and a broad shoulder at ~470 nm (ϵ ~10^3 M^{-1} cm^{-1}). These are undoubtedly the transitions mainly responsible for preresonance enhancement. Inasmuch as in $Fe(CO)_5$ the electronic transitions are at and above 244 nm,[30] the lower energy transitions of $S_2Fe_2(CO)_6$ are ascribable largely to the S_2Fe_2 cluster. It is entirely resonable that the cluster vibrational modes are the ones to experience enhancement of the Raman intensity. It would be interesting to explore this resonance effect further, using excitation within the absorption bands. Our attempts to do this have so far been frustrated by decomposition of the sample.

Conclusions

Both the frequencies and Raman intensities of the A_1 modes of $S_2Fe_2(CO)_6$ are satisfactorily accounted for with a simple valence force field and one (Fe–S, S–S) interaction constant. The magnitudes of the force constants are all reasonable and in particular f_{Fe-Fe} = 1.3 ± 0.2 mdyn/Å is satisfactory for an iron–iron single bond. The modes primarily associated with vibrations of the S_2Fe_2 cluster display preresonance Raman enhancement, which is probably associated with cluster electronic transitions in the visible and near-ultraviolet regions.

Registry No. $S_2Fe_2(CO)_6$, 14243-23-3; *syn*-$(CH_3S)_2Fe_2(CO)_6$, 19976-88-6; *anti*-$(CH_3S)_2Fe_2(CO)_6$, 19976-87-5.

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Photoelectron Spectra of Substituted Benzenes. III. Bonding with Group V Substituents

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The electronic structure of the group V phenyl compounds $C_6H_5XH_2$ where X = N or P, $(C_6H_5)_2XH$ where X = N, P, or As, and $(C_6H_5)_3X$ where X = N, P, As, or Sb has been investigated through the use of He(I) photoelectron spectroscopy and CNDO/2 MO calculations. The spectra of benzylamine and dichloro- and dimethylphenylphosphine and the He(II) spectra of phenylphosphine have also been obtained in order to assist in identification and assignment of the above series. The results show that the nitrogen nonbonding orbital in the phenylamines is more tightly bound then the phenyl π orbitals while in the phenylphosphines, -arsines, and -stibine the nonbonding orbital is at lowest binding energy. The destabilization of the n orbital and stabilization of the π orbitals in the P, As, and Sb molecules relative to the N molecules are taken as evidence for a shift of electron density from the phenyl groups toward the P, As, and Sb atoms. These shifts suggest that the heavier central atoms are capable of using expanded basis sets which include *n*d orbitals in the molecular bonding.

Introduction

Sharp contrasts exist in the chemical properties of nitrogen compounds as compared to those of other group V compounds. The most common explanation for these differences is the capability of expansion of the valence shells in the third-, fourth-, and fifth-row elements in order to accommodate extra electron density. The nitrogen atom has only the 2s and 2p atomic orbitals available for bonding while the heavier atoms have *n*s, *n*p, and *n*d orbitals available. The question of if and when these *n*d orbitals partake in bonding has been a subject of much debate.

Evidence for and against d-orbital participation in aromatic compounds containing group V atoms has been presented. Much of this evidence has come from studies of ultraviolet absorption spectra. The absorption spectra of the phenylamines, -phosphines, and -arsines have been studied by several workers.[1-9] These spectra exhibit band structure in the near-ultraviolet region (200–300 mμ), the identity of which remains unsolved. Some of the most convincing interpretations[1,9] have proposed intense n → π^* and weak $\pi \to \pi^*$ benzene-like transitions in this region. The participation of d orbitals in the transitions has been suggested by several of these authors. Bissey and Goldwhite[2] claimed that their application of the "substitution interference method" of Goodman, *et al.*,[10,11] provides positive evidence for d-orbital participation in the bonding of phenylphosphine.

The implication of d-orbital participation in bonding through shifts observed in absorption spectra can be misleading, for it is difficult to determine whether the shifts are caused by a stabilization of the initial or final state involved in the transition. Since photoelectron spectroscopy is based on an absolute energy scale, it is possible to estimate the degree of d-orbital participation through shifts in the binding energies of occupied molecular orbitals in the ground state. Shifts in the binding energies of certain orbitals have been used as evidence for d-orbital participation in the bonding of some group IV[12-15] and organometallic phosphorus[16] compounds.

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The He(I) photoelectron spectra of the group V phenyl compounds $C_6H_5XH_2$ where X = N or P, $(C_6H_5)_2XH$ where X = N, P, or As, and $(C_6H_5)_3X$ where X = N, P, As, or Sb have been measured. The spectra of benzylamine and dichloro- and dimethylphenylphosphine and the He(II) spectrum of phenylphosphine have also been obtained to assist in the identification of certain ionization bands. The high-resolution spectrum of aniline has been assigned[17] in our previous work using a composite-molecule approach.[18] Assignment of the ionization bands has been facilitated by the use of the composite-molecule approach, intensity changes upon phenyl substitution, the He(II) effect, and CNDO/2 MO calculations.[19] Shifts in the binding energies of certain orbitals have been investigated in order to determine the extent of d-orbital participation in the molecular bonding.

Experimental Procedure

The spectra were recorded on a Perkin-Elmer Model PS-16 photoelectron spectrometer modified with a heated-probe inlet system. The He(I) resonance line at 584 A (21.22 eV) served as the ionizing source. Most of the samples studied have low vapor pressures and had to be heated in order to produce sufficient vapor for obtaining good electron fluxes. The temperature of the collision chamber was monitored by a thermocouple placed ~1 cm above the chamber slit. Although the thermocouple was in thermal contact with the walls of the collision chamber and the temperature could be maintained within ±1.0° for extended periods, the actual temperature of the gaseous molecules may deviate from the measured temperature significantly due to thermal gradients. The temperatures at which the spectra were recorded were those which gave the best balance between electron flux and sample stability.

All compounds studied were commercially available reagent grade chemicals. The organophosphorus and -arsenic compounds were obtained from Pressure Chemical Co. and the phenylamines and triphenylstibene were obtained from J. T. Baker Chemical Co. The spectra were calibrated by use of the Ar $^2P_{3/2}$ (15.759 eV) and $^2P_{1/2}$ (15.937 eV) lines and Kr $^2P_{3/2}$ (13.999 eV) and $^2P_{1/2}$ (14.665 eV) lines as internal standards with a resulting calibration precision of ±0.01 eV.

Results

The photoelectron spectra of phenylamine, -phosphine, -arsine, and -stibine compounds are shown in Figure 1. The ionization energies and intensities of the observed bands are listed in Table I. The following observations have been made from these spectra. (i) All of the spectra exhibit three ionization regions between 7 and 11 eV. (These regions are overlapping in phenylphosphine.) Most of the di- and triphenyl compounds have irregular shoulders on the second band which appear to be due to overlapping transitions. (ii) Upon successive replacement of hydrogens by phenyl groups, the first and third ionization regions shift to lower binding energy while the second region remains stationary at ~9 eV. (iii) Upon successive replacement of hydrogens by phenyl groups, the intensity of the first and second regions of the nitrogen compounds increases with respect to the third region while in the phosphorus, arsenic, and stibene compounds the relative intensity of the second and third regions increases with respect to the first.

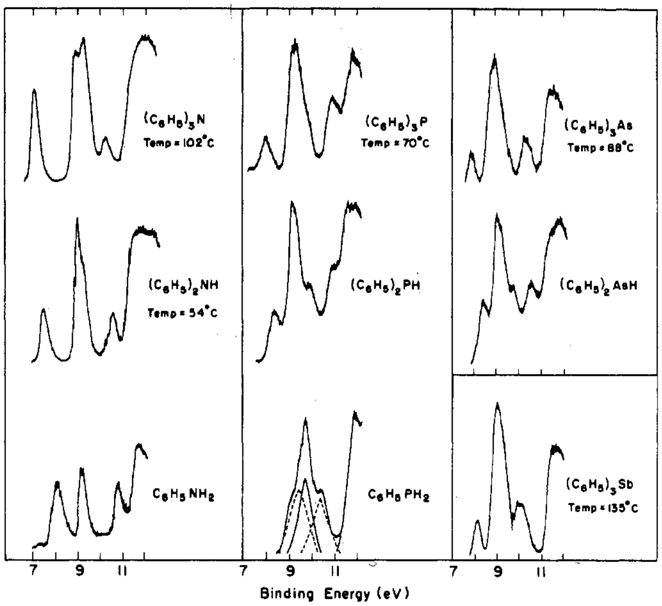

Figure 1. The He(I) photoelectron spectra of the low-energy ionization bands of some phenylamines, -phosphines, -arsines, and -stibine.

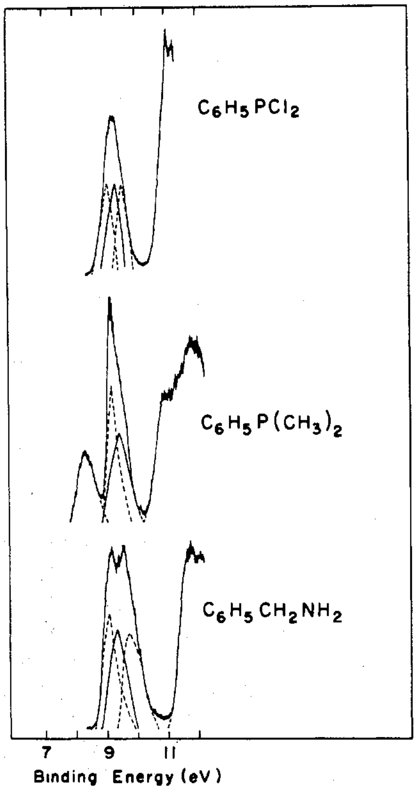

Figure 2. The He(I) photoelectron spectra of the low-energy ionization bands of benzylamine and dichloro- and dimethylphenylphosphine.

The spectra of dichloro- and dimethylphenylphosphine and benzylamine are illustrated in Figure 2 and the experimental IP's are listed in Table I. (i) Only one broad, intense band exists in the low-energy region of dichlorophenylphosphine. This region appears to consist of three overlapping ionization bands. The intense bands centered at ~11.5 eV are due to ionization of chlorine nonbonding electrons. (ii) The spectrum of dimethylphenylphosphine shows a band at 7.81 eV, a very intense band at 8.83 eV, and a weaker shoulder at 9.16 eV. (iii) The low-energy region of the benzylamine spectrum shows a broad, intense band with two clear maxima at 9.10 and 9.30 eV and a shoulder at 9.70 eV.

The He(I) (21.2 eV) and He(II) (40.8 eV) excited photo-

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Table I. Ionization Potentials and Electronic Assignment of Ionization Bands

IP	Assignment	Energy, eV	Rel intens	Energy, eV	Rel intens	Energy, eV	Rel intens
		Aniline		Diphenylamine		Triphenylamine	
1	π	7.71 (A)[b]	1.0	7.18 (A)	1.6	6.75 (A)	1.7
		8.02 (V)[b]		7.35 (V)		6.99 (V)	
2	π	8.94 (A)	1.0	8.75 (A)	3.7	8.69 (A)	2.2
		9.12 (V)		9.00 (V)		8.80 (V)	
						9.21 (V)	3.2
3	n	10.45 (A)	1.0	10.18 (A)	1.0	10.27 (V)	1.0
		10.78 (V)		10.56 (V)			
4	σ	11.9 (V)		11.0 (A)			
				11.7 (V)			
		Phenylphosphine		Diphenylphosphine		Triphenylphosphine	
1	n	8.47 (A)	1.1	7.80 (A)	1.0	7.37 (A)	1.0
		9.18 (V)[a]		8.29 (V)		7.88 (V)	
2	π	9.66 (V)[a]	1.1	9.08 (V)	4.8	8.71 (A)	4.6
						9.25 (V)	
3	π	10.32 (V)[a]	1.0	9.84 (V)	1.2	10.27 (A)	2.1
						10.90 (V)	
4		11.22 (A)		10.90 (V)	1.4		
		11.77 (V)					
5		12.3 (V)					
		Diphenylarsine		Triphenylarsine		Triphenylstibine	
1	n	7.87 (A)	1.0	7.60 (A)	1.0	7.80 (A)	1.0
		8.43 (V)		7.95 (V)		8.18 (V)	
2	π	9.06 (V)	4.2	8.38 (A)	5.3	8.50 (A)	6.2
				8.90 (V)		9.14 (V)	
3	π	9.78 (V)	1.2	9.78 (A)	1.6	10.09 (V)	3.4
				10.40 (V)			
4	π	10.56 (V)	1.3				
		Benzylamine		Dichlorophenylphosphine		Dimethylphenylphosphine	
1		9.10[a]	1.9 (π)	9.10 (A)	1,2 (n(P))	7.81 (A)	1.5 (n)
				9.63 (V)		8.31 (V)	
2		9.30[a]	2.0 (π)	9.88 (V)	1.1 (π)	8.60 (A)	1.6 (π)
						8.83 (V)[a]	
3		9.70[a]	2.1 (n)	10.13 (V)	1.1 (π)	9.15 (V)[a]	1.8 (π)
4				11.50 (V)	(n(Cl))		
5				11.67 (V)	(n(Cl))		

[a] Values obtained by deconvolution of overlapping bands. [b] A = adiabatic IP; V = vertical IP.

electron spectra of the low-energy bands of phenylphosphine are shown in Figure 3.

Quantum Chemical Considerations

CNDO/2 calculations[19] were performed on aniline and phenylphosphine in order to assist in understanding the electronic interaction in the outer molecular orbitals. Koopmans' theorem[20] was used in comparing calculated eigenvalues to experimental ionization potentials. In order to correct for the deficiencies in Koopmans' theorem, the π and n (p_z, π-type orbital) eigenvalues are empirically reduced by 20%. As discussed previously,[17,18,21] this provides a first-order correction to the improper positioning of the CNDO/2 σ and π manifolds relative to each other. The eigenvalues for aniline and phenylphosphine are plotted in Figure 4 as a function of the H plane of elevation. Only the π, n, and lowest energy σ orbitals are included. A serious deficiency of these calculations for aniline is the improper positioning of the π and σ manifolds relative to each other.

The dependence of the molecular orbitals on the H plane of elevation is an important feature when considering electron densities. In aniline and phenylphosphine, the $\pi(b_1)$ component of the split phenyl $\pi(e_{1g})$ orbital becomes partially delocalized in the substituent orbitals while the $\pi(a_2)$ component with a node at this point remains localized on the phenyl ring.[22] In both aniline and phenylphosphine two choices are possible for the nonbonding orbital, the in-plane p_y orbital or the out-of-plane p_z orbital. When the system is planar ($\theta = 90°$) the p_z orbital conjugates with the $\pi(b_1)$ ring orbital but the electron density on the X atom remains high. In this configuration p_y is a bonding σ orbital. As the H plane is brought to a perpendicular position ($\theta = 0°$), the p_y orbital becomes more nonbonding while the p_z orbital becomes more bonding. There are thus two possibilities for the nonbonding orbital, depending on the exact configuration of the molecules. Since the structure of aniline and phenylphosphine in the ground state is somewhere intermediate between these two extremes, the σ-π separability of the MO's is no longer possible. The so-called nonbonding orbital in these molecules is really an orbital with weak bonding character.

The MO calculations predict two major differences between the orbitals of aniline and phenylphosphine. (i) The relative positions of the π and n orbitals in the two systems are reversed. (ii) The relative positions of the $\pi(b_1)$ and $\pi(a_2)$ orbitals in the two systems are reversed. These differences are a result of interaction between the phosphorus p_z orbital and the ring $\pi(b_1)$ orbital which tends to destabilize the p_z orbital and stabilize the $\pi(b_1)$ orbital. This interaction is not as strong in aniline. The calculations indicate a greater charge density on the P atom (0.86, $\theta = 90°$) than on the N atom (0.52, $\theta = 90°$). This is unexpected from electronegativity considerations. It is apparent that electron density at the P atom is gained at the expense of the ring π orbi-

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(22) The MO's of aniline and phenylphosphine are identified by symbols from the C_{2v} point group although these molecules possess only gross C_{2v} symmetry.

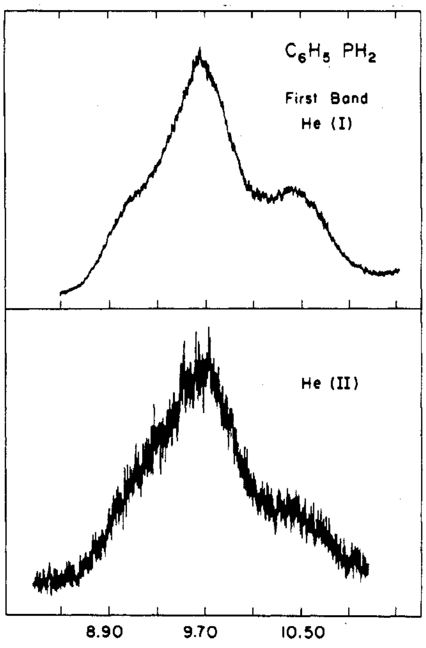

Figure 3. The He(I) and He(II) photoelectron spectra of the low-energy ionization bands of phenylphosphine.

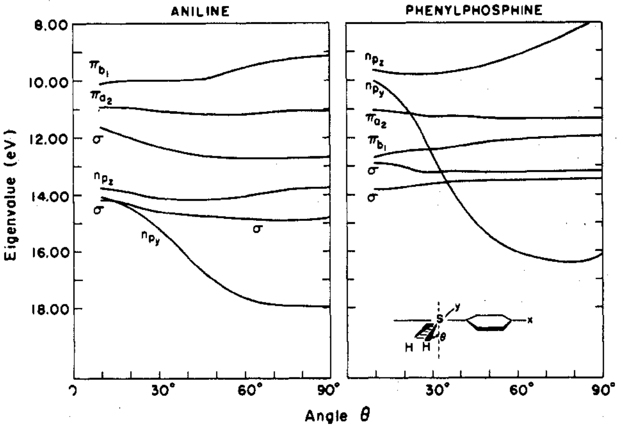

Figure 4. CNDO/2 eigenvalues for the π, n, and outermost σ orbitals of aniline and phenylphosphine plotted as a function of θ, the hydrogen plane of elevation (see text for discussion).

tals resulting in stabilization of the interacting $\pi(b_1)$ components and destabilization of the phosphorus n orbital.

This high electron density at the P atom is possible through the use of its 3d orbitals in the bonding scheme. The MO calculations indicate up to ~3% d-orbital character in some of the MO's.[23] The most important d orbitals in this interaction are the d_{xz} and d_{xy} orbitals. The d_{xz} and p_z atomic orbitals form the out-of-plane n orbital which has a favorable overlap with the $\pi(b_1)$ ring orbital. The d_{xy} and p_y atomic orbitals form the in-plane n orbital which overlaps with the σ orbitals of the ring. Thus, the d orbitals allow a flow of electron density from the phenyl groups to the P atom. The corresponding amine compounds do not have these low-energy virtual d orbitals which can accommodate extra charge.

Discussion

Assignments. Assignment of the spectral bands in the low-energy region was accomplished by reference to the previous work on aniline and by use of spectral band intensities. In our earlier work on aniline,[17] the three low-energy bands were identified as $n > \pi(a_2) > \pi(b_2)$ in order of decreasing binding energy. The replacement of hydrogen atoms by phenyl groups in ammonia results in an increase in the number of occupied π orbitals, *e.g.*, aniline 3π orbitals, diphenylamine 6π orbitals, and triphenylamine 9π orbitals. Since the intensity of photoelectron bands is roughly proportional to their occupancy, the increase in the number of occupied π orbitals will cause an increase in the number of π ionization bands. This explains the increase in intensity of the two low-energy ionization regions in the aniline series with respect to the third region. The region of di- and triphenylamine centered at ~9 eV exhibits shoulders that are due to these extra π ionization bands. The effect confirms our previous assignment[17] of the outermost bands of aniline.

This assignment of the bands in aniline is also supported by the study of benzylamine. Placing a methylene group between the amine group and the phenyl ring results in decoupling of the resonance interaction between the ring $\pi(b_1)$ orbital and nitrogen n orbital. The π orbitals remain near the position of those in toluene and the n orbital shifts to approximately its position in methylamine. The two intense peaks and the shoulder in this region of the benzylamine spectrum account for these three bands.

In the phenylphosphines, -arsines, and -stibine, the relative intensity of the second and third bands increases with respect to the first upon successive replacement of hydrogens by phenyl groups indicating that the n orbital is at lowest binding energy. This low-energy region of phenylphosphine was studied with He(II) excitation. The ionization cross sections for sulfur and phosphorus 3s and 3p orbitals are much less than those of carbon 2s and 2p orbitals when excited with He(II) radiation.[24] In this vein a drastic reduction in the ionization cross sections of certain bands upon changing from He(I) to He(II) radiation has been presented as proof of ionization of electrons from phosphorus 3s and 3p orbitals.[24,25] When He(II) radiation is applied to phenylphosphine, Figure 3, the intensity of the low-energy shoulder decreases only very little with respect to the central and high-energy bands. This slight decrease in the intensity of the low-energy band suggests its identification as the phosphorus n orbital. The fact that its intensity did not decrease as drastically as observed in some other phosphorus compounds[25] indicates that it is not pure phosphorus in character.

The identification of the low-energy bands in the P, As, and Sb compounds was also assisted by the study of dichlorophenylphosphine and dimethylphenylphosphine. Upon chlorine substitution the outermost band shifts to higher energy while upon methyl substitution it shifts to lower binding energy. Considering the electron-withdrawing properties of chlorine and the electron-donating properties of the methyl groups, the observed behavior is that expected for the n orbital. It will be noted that the π orbitals shift slightly, but not as much as the n orbital, upon chlorine or methyl substitution.

The results of intensity considerations, the He(II) effect,

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(23) L. Pauling and M. Simonetta, *J. Chem. Phys.*, 20, 29 (1952), have shown that 2% d-orbital participation in the P_4 molecule can produce as much as 10 kcal/mol stabilization energy. It should also be noted that d-orbital participation is generally exaggerated by CNDO calculations.

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(25) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, 94, 1451, 1466 (1972).

and substitution effects all point to the assignment of the outer bands of the P, As, and Sb compounds as $\pi(a_2) > \pi(b_1) > n$ in agreement with the CNDO/2 calculations. The spectra of the P, As, and Sb compounds bear a close resemblance to that of nitrosobenzene whose outer MO configuration was determined[18] to be identical with that given above.

Orbital Energies. A shift toward lower binding energy upon successive replacement of hydrogens by phenyl groups occurs in the family of amines, phosphines, or arsines. This is a direct result of the better electron-donating properties of the phenyl group with respect to the hydrogen atoms. The relative orderings of the n and π orbitals of the amines with respect to the phosphines, arsines, and stibine must be considered. The shifts in the outer orbitals of the N, P, As, and Sb compounds are illustrated in Figure 5. Based on electronegativity considerations one would expect the binding energy of the n orbital to decrease in the order N > P > As > Sb. The observed ordering is N > Sb > As > P. This destabilization of the n orbital, along with the stabilization of the π orbitals, in the phosphines, arsines, and stibine relative to the amines indicates a shift of electron density from the phenyl groups toward the P, As, or Sb atom. This shift of electron density may be due to the ability of P, As, and Sb to expand their basis sets. These atoms have empty low-energy d orbitals into which the phenyl π electrons are capable of delocalizing. The CNDO/2 results indicate overlap of the phosphorus d_{xz} and d_{xy} orbitals with the adjacent carbon $2p_z$ and $2p_y$ orbitals providing a link for electron density shifts from the phenyl ring to the P, As, or Sb.

The stabilization of the n orbital in the phenylarsines relative to the phenylphosphines and in triphenylstibine relative to triphenylarsine indicates that electron density at the central atom decreases in the order P > As > Sb. This may be a result of the less effective overlap of the *n*d orbitals of the heavier atoms with the carbon 2p orbitals. The increase in electron density at the phosphorus atom with successive addition of phenyl groups by the d-orbital mechanism suggested here is supported by the reactivities[26] of the $(C_6H_5)_nP$ molecules. For example, the basicity and nucleophilicity of triphenylphosphine[27] result in the most probable electrophilic attack taking place at the phosphorus atom whereas in phenylphosphine the most probable reaction is ring substitution. The high electron density at the phosphorus atom also accounts for the good ligating properties of triphenylphosphine.

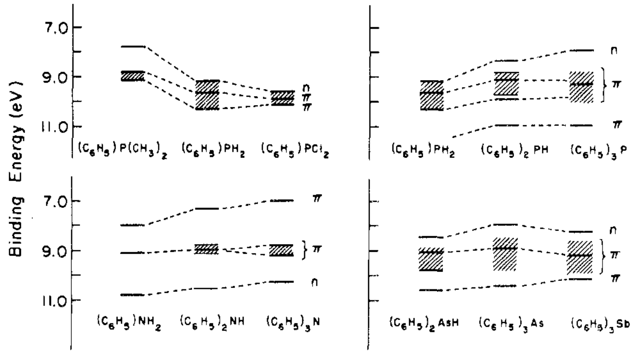

Figure 5. Correlation of observed ionization bands. The horizontal lines within the hatched areas correspond to the maxima of broad bands.

Conclusion

The analysis of the photoelectron spectra of some group V phenyl compounds coupled with CNDO/2 MO calculations has provided information on the electronic structure of these systems. Changes in molecular bonding have been studied as a function of the increasing size of the central atom, X, in $(C_6H_5)_nX$ type systems. The analysis of the results indicates that the nonbonding electrons of the central atom reside in the most loosely bound orbital for X = P, As, and Sb but are more tightly bound for X = N. The stabilization and destabilization of certain orbitals suggests the expansion of the valence shell of P, As, and Sb to include *n*d orbitals in the molecular bonding.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. $C_6H_5NH_2$, 62-53-3; $(C_6H_5)_2NH$, 122-39-4; $(C_6H_5)_3N$, 603-34-9; $C_6H_5PH_2$, 638-21-1; $(C_6H_5)_2PH$, 829-85-6; $(C_6H_5)_3P$, 603-35-0; $(C_6H_5)_2AsH$, 829-83-4; $(C_6H_5)_3As$, 603-32-7; $(C_6H_5)_3Sb$, 603-36-1; $C_6H_5CH_2NH_2$, 100-46-9; $C_6H_5PCl_2$, 644-97-3; $C_6H_5P(CH_3)_2$, 672-66-2.

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