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Measured Binding Energy Shifts of the "3p" and "3d" Electrons[1] in Arsenic Compounds

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X-Ray photoelectron spectroscopy was used to determine chemical shifts in the binding energies of electrons in the "3p" and "3d" orbitals of 32 arsenic compounds. The resulting binding-energy shifts are discussed in terms of the influence of atoms directly bonded to the arsenic. The usual trend of an increase in binding energy with increasing substituent electronegativity was observed. Analogous nitrogen, phosphorus, and arsenic chemical environments were compared both experimentally and theoretically, with the aid of atomic SCF calculations, to determine the relative chemical shifts. Some data are also presented on the effects of using different referencing compounds.

Introduction

In order for X-ray photoelectron spectroscopy of inner-orbital electrons to be utilized to its full potential in chemical applications, a large number of measurements must be taken on a wide range of compounds of various atoms[2-8] throughout the periodic table. This work not only includes chemical shift data on a series of compounds of a little-studied atom but also introduces a particularly interesting comparison of the chemical shifts of similar group V compounds of nitrogen, phosphorous, and arsenic.

The theoretical concepts utilized in X-ray photoelectron spectroscopy have become well known since its recently established practicability.[8] The conservation relationship between the kinetic energy E_{kin} of the ejected electron with binding energy E_{b} and the energy of the X-radiation $E_{\text{X-ray}}$ is

$$E_{\text{b}} = E_{\text{X-ray}} - E_{\text{kin}} - \phi_{\text{sp}} \qquad (1)$$

where the constant ϕ_{sp} is the work function of the spectrometer material (generally aluminum).

Experimental Section

Three independent photoelectron spectrometers were utilized in the present investigation and all three gave comparable results. Two identical instruments yielded the main body of information. Both were Varian Induced-Electron-Emission (IEE) spectrometers, employing electrostatic electron analyzers and μ-metal shielding for isolation from external magnetic fields. The entire operation of these instruments is controlled through the Varian 260/i digital computer with a 4K memory. Instrument resolution at an analyzer energy of 100 eV corresponds to less than 2.0 eV full peak width at half-height for the carbon "1s" electron of graphite. The other instrument employed was an iron-free double-focusing magnetic spectrometer which has been described in detail elsewhere.[9] In all cases, photoionization of the electrons was accomplished with the use of Al Kα X-radiation (1486.6 eV) which contributes 0.8 eV to the observed line width.

Each of the instruments was found to give excellent agreement ($\pm$0.2 eV) for the binding energies of the "3p" and "3d" arsenic electrons present in $(C_6H_5)_3As$, as referenced to the carbon "1s" line for which a value of 285.0 eV was assumed. This method of "internal" referencing was shown to be useful in previous work.[6] By precisely measuring the kinetic energy of the electrons photoejected from a given sample and supplying the remaining constants to eq 1, the binding energy is obtained directly. This "direct" measurement was found to be remarkably reproducible on the Varian IEE spectrometer because of its excellent magnetic shielding and the constant X-ray flux produced at the consistent settings of 8 KV and 70 mA and the low-pressure conditions of $<2 \times 10^{-6}$ Torr. Individual measurements on two separate units (one in Palo Alto, Calif., the other in St. Louis, Mo.) yielded standard deviations of *ca.* $\pm$0.5 eV between the instruments. The reproducibility of a single spectrometer was determined by measuring the carbon "1s" (graphite), carbon "1s" (adsorbed hydrocarbon vapor), and the gold doublet "4f" lines for several days during 2 separate weeks (1 month apart) of experimental measurements, producing a standard deviation of less than $\pm$0.2 eV. This fact eliminated the necessity for replicate measurements to be reported on each individual compound, in sharp contrast to some other spectrometers, for example, the instrument at Vanderbilt where, from direct measurements on a solid, a given binding energy may vary by as much as 2 eV over a period of days.

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(1) The atomic orbital designations are put in quotation marks since the inner orbitals are somewhat delocalized in the compounds; however, they may be conveniently referred to in this manner.

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(9) A. Fahlman, R. G. Albridge, R. Nordberg, and W. M. LaCasse, *Rev. Sci. Instrum.*, **41**, 596 (1970).

Table I

Experimental Binding Energies of Various Arsenic Compounds

No.	Compd	Coord no.	Mean electronegativity diff		Measd binding energy, eV						
					C "1s"	As "$3p_{1/2}$"		As "$3p_{3/2}$"		As "3d"	
					Direct	Direct	Cor	Direct	Cor	Direct	Cor
1	$LiAsF_6$	6	2.0			156.4	151.5	152.2	147.3	53.2	49.3
					289.9	156.7	151.8	152.7	147.8		
					287.6^{a}						
										52.2^{a}	49.6^{a}
										52.5^{d}	48.9^{d}
										53.3^{d}	49.2^{d}
										53.1^{e}	
										52.8^{e}	
										52.7^{e}	
				Av	288.8 ± 1.6	156.6 ± 0.2	151.7 ± 0.2	152.5 ± 0.4	147.6 ± 0.4	52.8 ± 0.4	49.3 ± 0.3
2	$KAsF_6$	6	2.0		288.8					52.1	48.3
							151.3^{b}		146.6^{b}		47.3^{b}
									147.0^{b}		48.1^{b}
				Av					146.8 ± 0.3		47.9 ± 0.5
3	$(C_6H_5)_3CAsF_6$	6	2.0		285.4	151.0	150.6	146.5	146.1		
							152.3^{b}		146.8^{b}		48.5^{b}
				Av			151.5 ± 1.2		146.5 ± 0.5		
4	As_2O_5	4	1.5		286.7	152.2	150.5	147.4	145.7	48.4	46.7
							149.6^{b}		145.3^{b}		46.0^{b}
				Av			150.1 ± 0.6		145.5 ± 0.3		46.4 ± 0.5
											46.6 ± 0.4^{c}
5	As_2O_3	3	1.5		286.2	151.2	150.0	146.8	145.6	47.8	46.6
					287.2					48.6	46.4
					287.5^{a}					47.8^{a}	45.3^{a}
										48.3^{d}	45.9^{d}
										47.8^{e}	
										48.1^{e}	
										48.0^{e}	
				Av	287.0 ± 0.7					48.1 ± 0.3	46.0 ± 0.6
											45.2 ± 0.2^{c}
6	$Na_4As_2O_7$	4	1.5		287.4	151.6	149.2	146.9	144.5	48.0	45.6
					287.1^{a}	151.5^{a}	149.4^{a}	146.5^{a}	144.4^{a}	47.6^{a}	45.5^{a}
										48.0^{d}	45.7^{d}
										46.6^{f}	
				Av	287.3 ± 0.2	151.6 ± 0.1	149.3 ± 0.1	146.7 ± 0.3	144.5 ± 0.1	47.6 ± 0.7	45.6 ± 0.1
7	KH_2AsO_4	4	1.5		287.3	151.6	149.3	147.1	144.8	49.2	46.9
8	$Na_2HAsO_4 \cdot 7H_2O$	4	1.5		287.3	151.2	148.9	146.5	144.2	47.4	45.1
9	Na_3AsO_4	4	1.5		287.5	150.7	148.2	145.6	143.1		
					286.8^{a}			145.5^{a}	143.7^{a}	46.9^{a}	45.1^{a}
									143.6^{b}		44.0^{b}
				Av	287.2 ± 0.5			145.6 ± 0.1	143.5 ± 0.3		44.6 ± 0.8
10	K_3AsO_4	4	1.5		287.1	150.5	148.4	146.0	143.9	46.7	44.6
									144.0^{b}		45.7^{b}
				Av					144.0 ± 0.1		45.2 ± 0.8
11	$(o\text{-}NH_2C_6H_5)AsO(OH)_2$	4	1.3		285.7	150.3	149.6	145.5	144.8	46.8	46.1
12	$(C_6H_5)AsO(OH)_2$	4	1.3			150.8		146.1			
					284.9^{a}	150.2^{a}	150.3^{a}	145.3^{a}	145.4^{a}	46.2^{a}	46.3^{a}
				Av		150.5 ± 0.4		145.7 ± 0.6			
											46.1 ± 0.2^{c}
13	$(p\text{-}OHC_6H_5)AsO(OH)_2$	4	1.3		286.3	150.9	149.6	145.9	144.6		
14	$(p\text{-}NH_2C_6H_5)AsO(OH)_2$	4	1.3		286.0	149.5	148.5	145.3	144.3	46.3	45.3
15	$(CH_3)_2AsO(OH)$	4	1.0		287.6	151.9	149.3	147.1	144.5		
							148.4^{b}		144.0^{b}		45.1^{b}
				Av			148.9 ± 0.6		144.3 ± 0.4		
											44.7 ± 0.7^{c}
16	$As_4(NCH_3)_6$	3	1.0		287.9	151.7	148.8	147.0	144.1		
17	$(C_6H_5)_3As(OH)_2$	5	0.9		285.2	148.9	148.7	143.9	143.7	44.9	44.7
18	$NaAsO_2$	4	0.8		287.3	150.9	148.6	145.9	143.6		
19	$[(C_6H_5)_3AsO]_2HgCl_2$	4	0.8		285.5	148.7	148.2	144.5	144.0	45.5	45.0
20	$(C_6H_5)_3AsO$	4	0.8		285.0	148.4	148.4	143.0	143.0	44.5	44.5
					285.5	148.5	148.0	144.1	143.6	45.2	44.7
					284.9					44.3	44.4
									143.3^{b}		44.7^{b}
											44.8^{b}
				Av	285.1 ± 0.3	148.5 ± 0.1	148.2 ± 0.3	143.6 ± 0.8	143.3 ± 0.3	44.7 ± 0.5	44.6 ± 0.2
21	$AsBr_3$	3	0.8		285.0	150.4	150.4	145.9	145.9		
22	$(C_6H_5)_4AsBr$	4	0.5		284.9	148.8	148.9	143.7	143.8	44.8	44.9
23	$(C_6H_5)_4AsCl$	4	0.5		285.0	148.3	148.3	143.8	143.8		
24	As_2S_5	4	0.5		285.0^{a}	148.9^{a}	148.9^{a}	144.2^{a}	144.2^{a}	44.6^{a}	44.6^{a}
										46.3^{d}	43.9^{d}
										45.2^{e}	
										44.9^{e}	
										44.3^{e}	
				Av						45.1 ± 0.8	44.3 ± 0.5
25	As_2S_3	3	0.5		287.1	150.1	148.0	145.0	142.9		43.7 ± 0.2^{c}
26	$(C_6H_5)_3As$	3	0.5		285.2	146.8	146.6	142.2	142.0	43.2	43.0
					284.7	146.5	146.8	141.8	142.1	42.8	43.1
					284.4^{a}					42.7^{a}	43.3^{a}
									142.1^{b}		43.1^{b}
										44.5^{d}	43.2^{d}
					284.9^{f}					43.3^{f}	43.4^{f}
				Av	284.8 ± 0.4	146.7 ± 0.2	146.7 ± 0.1	142.0 ± 0.3	142.1 ± 0.1	43.3 ± 0.7	43.2 ± 0.2

TABLE I (*Continued*)

				Measd binding energy, eV						
			Mean electro-negativity	C "1s"	As "$3p_{1/2}$"		As "$3p_{3/2}$"		As "3d"	
No.	Compd	Coord no.	diff	Direct	Direct	Cor	Direct	Cor	Direct	Cor
27	$[(C_6H_5)_3As]HgCl_2$	4	0.4	285.8	149.5	148.7	143.8	143.0	44.9	44.1
28	$[(C_6H_5)_3As]_2HgI_2$	4	0.4	285.8	148.6	147.8	143.5	142.7	44.4	43.6
29	As_4S_4	3	0.3	286.0	148.8	147.8	144.2	143.2		
30	As	3	0.0	286.0					43.1	42.1
								141.1[b]		41.8[b]
	Av									42.0 ± 0.2[g]
31	Zn_3As_2		−0.3	288.7	147.3	143.6	144.1	140.4		
32	AlAs	4	−0.5	286.9	151.0	149.1	145.9	144.0		
						148.8[b]		144.1[b]		45.0[b]
	Av					149.0 ± 0.2		144.1 ± 0.1		

[a] Measurements made at Monsanto Chemical Co. on a Varian IEE spectrometer. [b] Measurements made on Vanderbilt spectrometer using residual carbon "1s" as reference. [c] L. D. Hulett and T. A. Carlson, *Appl. Spectrosc.*, **25**, 33 (1971). [d] Measurements made at Monsanto Chemical Co. referenced to Pb "$4f_{7/2}$" (138.3 eV) present in the mixture of Pb_3O_4 and the arsenic compound. [e] Measurements on the $LiAsF_6$–As_2O_3 and As_2S_5 mixture made at Monsanto Chemical Co. [f] Measurements on the $(C_6H_5)_3As$–$Na_4As_2O_7$ mixture made at Monsanto Chemical Co. [g] An additional oxidation peak appeared in all cases with a higher binding energy of approximately 3.0 eV.

Since all of the samples investigated were solids, the finely ground powders were mounted on plastic tape, having adhesive on both sides, which was attached to an aluminum sample holder. In all cases the carbon "1s" line from the adsorbed hydrocarbon vapors was measured for reference purposes. Additionally some of the samples were mixed with Pb_3O_4 and referenced to the "4f" electron doublet of the lead, the value of which was obtained by utilizing the previously determined value of the As "3d" for $(C_6H_5)_3As$, equal to 43.2 eV, in an intimate mixture of these two compounds.

Many of the arsenic compounds studied in this work were purchased. The remaining compounds were prepared by previously reported synthetic procedures[10–12] utilizing appropriate recrystallization techniques. All of the compounds represent materials of high purity.

Atomic *ab initio* SCF calculations[13] were applied to the arsenic, phosphorus, and nitrogen neutral atoms and +1 ions in their lowest (Hund's rule) energy states corresponding to various configurations of the valence electrons. A Slater basis set consisting of four "s," three "p," and three "d" (433) orbital exponents was used, with optimization of all exponents, to calculate the atomic orbital energies of the various arsenic atoms. A Slater (322) basis set was used for the corresponding phosphorus atoms while a Slater (211) basis set was found to describe adequately the necessary nitrogen atomic calculations. The outer-orbital configurations investigated were the following: s^2p^3 (^4S), sp^4 (^4P), s^2p^2d (^4F), sp^3d (^6D), s^2p^2 (^3P), sp^3 (^5S), s^2pd (^3F), and sp^2d (^5F). Wherever possible [*i.e.*, for As^+, s^2p^2 (^3P); P^0, s^2p^3 (^4S); P^+, s^2p^2 (^3P); N^0, s^2p^3 (^4S); N^+, s^2p^2 (^3P)] the total energies were compared with values from a tabulation of very accurate wave functions by Clementi[14] and were found in every case to give greater than 99.7% of the total energy.

Results and Discussion

The experimental values of the "3p" electron-doublet and the "3d" coalesced-doublet binding energies appear in Table I, listed according to decreasing electronegativity difference of the directly bonded substituents in the various arsenic compounds. Although the arsenic "$3p_{1/2}$"–"$3p_{3/2}$" doublet was observed to be present in the expected 1:2 ratio, the exact position of the more intense "$2p_{3/2}$" line may be more accurately determined and hence has been used in the various intercomparisons given below. The separation of these two peaks was found to be essentially constant at 4.7 ± 0.3 eV, with no consistent trends within the small range of variation; while the difference between the "3d" level and the midpoint of the "3p" doublet was also similarly constant at 101.2 ± 0.4 eV. The observed constancy in these measured differences exemplifies the fact that the binding energies of all of the inner orbitals of a given atom undergo essentially the same chemical shift from one compound to another so that the energy differences between these orbitals remain quite fixed. The value of 101.2 ± 0.4 eV for the experimental "3p"–"3d" difference agrees amazingly well with the respective Hartree–Fock orbital-energy difference[14] of 102.5 eV for the ground-state atom. Our SCF calculations using a Slater (433) basis set gave an average value of 102.4 ± 0.2 eV for all of the valence orbital configurations studied. The good agreement between the observed "3p"–"3d" difference and the respective SCF orbital-energy difference indicates an overall cancelation of the correlation, reorientation, and relativistic contributions[15] to this energy term.

The electronegativity differences appearing in Table I are average values obtained by summing the differences between the Pauling[16] electronegativity of arsenic and each atom directly bonded to arsenic and dividing by the coordination number of arsenic. This operation is more or less equivalent[17] to estimating the atomic charge on the arsenic in the respective compound. Previous discussions[4,18] have pointed out the arbitrary and wholly formal nature of quantum mechanical calculations of atomic charges. Thomas[18] found that a simple comparison of observed binding energies with the respective total electronegativity differences gave a satisfactory correlation. Since the more complicated population analysis procedure of assigning atomic charges from SCF calculations gives results which are only indicative and are not invariant

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(10) Oxidation of triphenylarsine by 30% hydrogen peroxide yielded $(C_6H_5)_3As(OH)_2$; see "Beilsteins Handbuch der organischen Chemie," Vol. 16, 4th ed, Springer-Verlag, Berlin, 1933, p 846.

(11) D. J. Phillips and S. Y. Tyree, *J. Amer. Chem. Soc.*, **83**, 1806 (1961), for $[(C_6H_5)_3AsO]_2HgCl_2$.

(12) R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940), for $[(C_6H_5)_3As]_2HgI_2$ and $[(C_6H_5)_3As]HgCl_2$.

(13) B. Roos, C. Salez, A. Viellard, and E. Clementi, "A General Program for Calculation of Atomic SCF Orbitals by the Expansion Method," IBM Research Laboratory, San Jose, Calif. 95114.

(14) E. Clementi, "Tables of Atomic Functions," a supplement to a paper appearing in *IBM J. Res. Develop.*, **9**, 2 (1965).

(15) W. G. Richards, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).

(16) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; the electronegativity values used were taken from Appendix 13 in ref 8.

(17) According to N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68**, 171 (1946), the charge, h_B, in the atomic orbitals of atom A due to an A–B bond is $h_B = 1.0 + 0.16(\chi_A - \chi_B) + 0.035(\chi_A - \chi_B)^2$, where χ_A represents the electronegativity of atom A. Since the term $0.035(\chi_A - \chi_B)^2$ is small with respect to the prior term in this equation, we see that h_B is about proportional to the electronegativity difference, $(\chi_A - \chi_B) = \Delta\chi$. The "charge" on an atom is obtained from Σh_{B_i}, so that it is approximately proportional to $\Sigma(\Delta\chi)$ for unionized molecules.

(18) T. D. Thomas, *J. Amer. Chem. Soc.*, **92**, 4184 (1970).

to the particular basis set used,[4,19] the simpler method of correlation with electronegativity differences seems preferable. Although a recently proposed definition[19] of the charge on an atom in a molecule is readily applied to linear molecules, the inherent arbitrariness of atomic charge definitions was not eliminated.

In Figures 1 and 2 the observed binding energies are correlated with the respective mean electronegativity differences. The lines in these figures result from a least-squares fit to all of the data. In accord with previous observations with main-group atoms exhibiting low-lying valence shell d orbitals, the points in these two figures are rather scattered. We have previously attributed this scatter for silicon compounds to p$\pi \rightarrow$ dπ feedback. However, the positions in the figures of the points for the tetraphenylarsonium ions (no. 22 and 23) and triphenylarsine (no. 26) are such that we cannot simply draw a line through them and say that the other points lie below this line by a distance dictated by the amount of electronic feedback into the "4d" orbitals of the arsenic. Note that in the figures the points for $AsBr_3$ (no. 21) and AlAs (no. 32) correspond to higher binding energies than would be expected. We infer from this that these two compounds had undergone surface hydrolysis or oxidation so that their observed binding energies approach that of the oxides (no. 5 for As_2O_3 and no. 4 for As_2O_5).

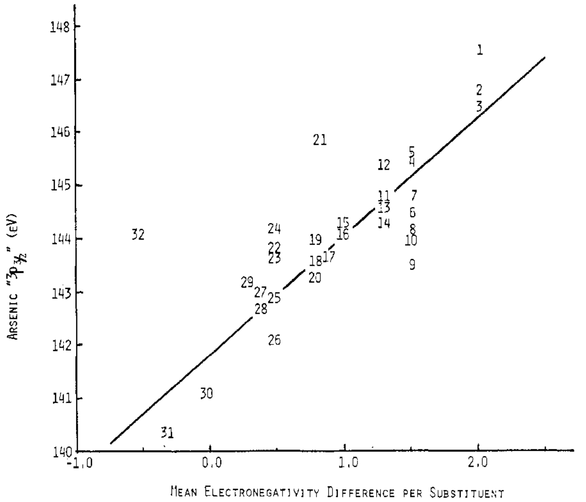

Figure 1.—The measured "$3p_{3/2}$" binding energies of various arsenic compounds *vs.* the average electronegativity difference of the substituents directly attached to arsenic. The binding-energy values are corrected by referencing to the hydrocarbon "1s" contaminant line (assuming a value of 285.0 eV). The solid line was obtained from a least-squares treatment of the data which are represented by the numbers of the corresponding arsenic compounds presented in Table I.

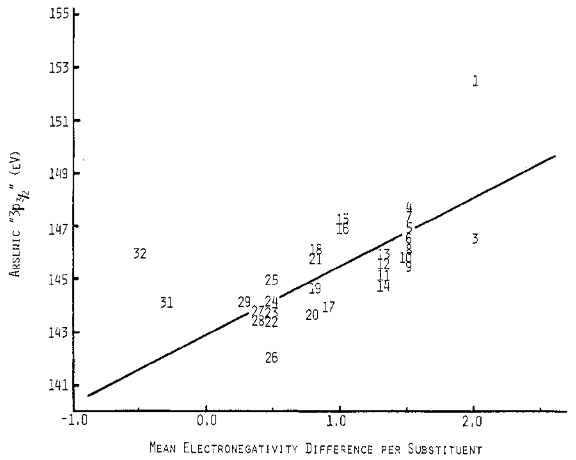

Figure 2.—The measured "$3p_{3/2}$" binding energies of various arsenic compounds *vs.* the average electronegativity difference of the substituents directly attached to arsenic. The binding-energy values utilized in this plot are direct (unreferenced) measurements. The solid line was obtained from a least-squares treatment of the data which are represented by the numbers of the corresponding arsenic compounds presented in Table I.

Plots corresponding to Figures 1 and 2 were prepared using the charge on the arsenic atom as the abscissa. These plots were not found to differ greatly overall from Figures 1 and 2 or with various estimations of the atomic charge. The main differences were found for points 22 and 23 which were shifted close to points 9 and 10, when the atomic charge was used as the abscissa, and for point 5 which was shifted slightly to the left-hand side of point 12.

Since the Varian IEE spectrometers used in this investigation were found to give high reproducibility in the directly measured binding energies as well as in the values corrected to some reference material, both kinds of experimental data are treated individually. It is significant to note that large differences in the corrected and direct measurements occur primarily in the compounds containing several highly electronegative substituents. The purpose of correlating the measurements by utilizing some well-known reference material is primarily to account for the charging-up effect[8,20] observed in insulators and semiconductors. Since the insulating sample is mounted in an evacuated chamber and irradiated by the X-rays passing through an aluminum window, an appreciable potential (relative to the walls of the chamber) may build up on the surface from the loss of the ejected electrons. A large number of electrons are present in the chamber besides those photoejected from the sample so that an equilibrium is set up between the chamber walls and the sample surface through this electron flux. Depending upon the sample, the surface charge can be as high as 3 or 4 eV,[21] producing considerable retardation of the ejected electrons so as to cause higher values of the binding energy to be recorded than actually exist. Fadley, *et al.*,[20] have shown that the charging effect is directly dependent upon the amount of X-ray flux causing photoionization of the electrons.

Although the usual method of utilizing a thin coating of adsorbed hydrocarbons (alternatively referred to as residual-hydrocarbon contaminant or "pump oil") as a measure of the surface-charge shift yields reproducible results, it seems highly possible that this necessarily thin surface coating (note that estimated mean escape depth[22] is less than 100 Å) could be affected by the type of surface upon which it resides, irrespective of the additional effects of surface charging. The possibility of such polarization[4] or other interaction on the hydrocarbon contaminant by the underlying compounds containing highly electronegative nearest-neighbor atoms cannot be overlooked since

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(19) P. Politzer and R. R. Harris, *J. Amer. Chem. Soc.*, **92**, 6451 (1970).

(20) C. S. Fadley, G. L. Geoffroy, S. B. M. Hagstrom, and J. M. Hollander, *Nucl. Instrum. Methods*, **68**, 177 (1969).

(21) C. R. Brundle, *Appl. Spectrosc.*, **25**, 8 (1971).

(22) W. N. Delgass, T. R. Hughes, and C. S. Fadley, *Catal. Rev.*, **4**, 179 (1970).

these compounds nearly always exhibit large shifts of the hydrocarbon-contaminant "1s" line. Indeed, it seems unlikely that particles of these compounds would consistently show relatively larger electrical charging of their surfaces than exhibited by similar compounds having less electronegative atoms adjacent to the atom losing the inner-shell electron.

An attempt to illuminate some aspects of this problem is shown in Table II. The values given therein represent the relative chemical shifts calculated by the indicated method of referencing. Most interesting are the results of mixing several of the compounds together and directly observing the relative differences in a single spectrum. A slight alteration of this approach consisted of placing alternating narrow bands of the individual compounds around the cylindrical sample holder. With one exception, both of these methods agree more closely with the individual direct measurements than with the standard method of using a residual-hydrocarbon reference! When Pb_3O_4 is mixed with the samples, the results agree well with the carbon-referenced values and also agree with the few measurements made by Hulett and Carlson[23] (compounds 4, 5, 12, 15, and 25 in Table I). In addition to using the usual residual-carbon reference, these investigators mixed KCl with the arsenic compounds, thereby utilizing the chloride line as a reference. They also made a few measurements by compressing the compounds into a platinum mesh in the hope of sufficiently grounding the sample to the spectrometer. They reported that all of these values agreed quite well with each other; further, these values were found to be consistent with the carbon-referenced values prepresented herein. Due to the extremely complicated nature of surface charging, further investigations are necessary for practical clarification of the problem.

TABLE II

VARIOUSLY CALIBRATED RELATIVE CHEMICAL SHIFTS (IN eV) OF SETS OF ARSENIC COMPOUNDS

Ref method	Three compd $LiAsF_6$–As_2O_3–As_2S_5 Δ	Δ	Two compd $Na_4As_2O_7$–$(C_6H_5)_3As$ Δ
Direct measurement	4.6	3.5	4.9
Residual carbon	3.4	1.5	2.5
Each other (mixed)	5.0 ± 0.4	2.9 ± 0.4	3.2
Each other (bands)	4.7	3.7	...
Pb_3O_4 (mixed)	4.0	2.0	2.5

To aid in the interpretation of the experimental measurements on arsenic, atomic SCF calculations were performed on several outer-electron configurations of arsenic, phosphorus, and nitrogen, as neutral atoms and as their 1+ ions, in an attempt to approximate the type of valence shell reorganization which occurs when these atoms are present in molecules. Theoretical predictions of inner-orbital ionization energies based on Koopmans' theorem,[15,24] which equates the absolute value of the Hartree–Fock eigenvalue to the respective binding energy, have been compared with the alternant and more realistic method of calculating the difference in total energy between the ground-state atom and the "hole"-state ion.[25,26] Although the SCF-difference calculations give somewhat better estimations of the experimentally measured value of an electron-binding energy, interpretations of chemical shifts based on simply equating the binding energy to the absolute value of the respective orbital energy have been successfully applied both to atoms[4,23,27] and to small molecules.[18,28,29] Of particular importance to investigators working in inner-orbital photoelectron spectroscopy is the effect of the chemical environment of a particular atom on each of the atomic energy levels. Table III shows the remarkably parallel changes produced in all of the inner-shell orbital energies by rearrangement and ionization of the arsenic valence electrons. Similar effects were observed in calculations of free-ion states of iodine[27] (I^- through I^{4+}) produced by successively ionizing the iodide ion. The experimentally observed iodine chemical shifts[27] were found to be the same for eight inner orbitals, from "2s" through "4d." Additionally, all of the calculations show the expected large variations in the valence-orbital energies upon changing from one outer-electron configuration to another.

TABLE III

DIFFERENCE IN ORBITAL ENERGY (IN eV) CALCULATED FOR VARIOUS ATOMIC CONFIGURATIONS FROM THAT OF ARSENIC IN THE GROUND STATE, s^2p^3 (^4S)

			Energy levels						
Atom	Outer confign	State	1s	2s	2p	3s	3p	3d	Av shift
As^0	sp^4	^4P	1.8	1.6	1.7	1.5	1.7	1.7	1.7 ± 0.1
As^0	s^2p^2d	^4F	6.9	6.3	6.3	6.5	6.5	6.1	6.4 ± 0.3
As^0	sp^3d	^6D	7.5	6.9	7.0	7.3	7.5	7.1	7.2 ± 0.3
As^+	s^2p^2	^3P	10.5	10.6	10.6	10.6	10.6	10.6	10.6 ± 0.0
As^+	sp^3	^5S	11.5	11.5	11.5	11.4	11.6	11.6	11.5 ± 0.1
As^+	s^2pd	^3F	14.1	13.4	13.5	13.7	13.6	13.4	13.6 ± 0.3
As^+	sp^2d	^5F	14.8	14.1	14.2	14.3	14.5	14.2	14.4 ± 0.3

Table IV gives pertinent, calculated orbital energies

TABLE IV

ATOMIC SCF CALCULATED ORBITAL AND TOTAL ENERGIES FOR VARIOUS CONFIGURATIONS OF ARSENIC, PHOSPHORUS, AND NITROGEN

			Energy, eV				
Atom	Outer confign	State	Total	1s	2p	3p	3d
As^0	s^2p^3	^4S	−60718.0			156.9	54.7
As^0	sp^4	^4P	−60709.9			158.6	56.4
As^0	s^2p^2d	^4F	−60708.0			163.4	60.8
As^0	sp^3d	^6D	−60703.9			164.4	61.8
As^+	s^2p^2	^3P	−60709.9			167.5	65.3
As^+	sp^3	^5S	−60706.5			168.6	66.3
As^+	s^2pd	^3F	−60696.2			170.6	68.1
As^+	sp^2d	^5F	−60691.6			171.4	68.9
P^0	s^2p^3	^4S	−9248.9		140.4		
P^0	sp^4	^4P	−9240.8		142.0		
P^0	s^2p^2d	^4F	−9241.6		147.7		
P^0	sp^3d	^6D	−9238.2		148.0		
P^+	s^2p^2	^3P	−9239.9		151.8		
P^+	sp^3	^5S	−9236.4		152.6		
P^+	s^2pd	^3F	−9229.8		156.1		
P^+	sp^2d	^5F	−9225.3		156.3		
N^0	s^2p^3	^4S	−1476.7	424.4			
N^0	sp^4	^4P	−1464.2	425.1			
N^0	s^2p^2d	^4F	−1465.8	439.6			
N^0	sp^3d	^6D	−1461.7	437.6			
N^+	s^2p^2	^3P	−1464.2	442.6			
N^+	sp^3	^5S	−1460.2	440.7			
N^+	s^2pd	^3F	−1441.9	459.2			
N^+	sp^2d	^5F	−1436.9	456.6			

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(23) L. D. Hulett and T. A. Carlson, *Appl. Spectrosc.*, **25**, 33 (1971).

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(25) P. S. Bagus, *Phys. Rev. A*, **139**, 619 (1965).

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(27) C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968).

(28) T. D. Thomas, *ibid.*, **52**, 1373 (1970).

(29) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *ibid.*, **52**, 3295 (1970).

of the various atomic configurations of arsenic, phosphorus, and nitrogen, as well as the respective total energies. The ordering of the atomic inner-orbital energies, arranged according to increasing energy, is slightly altered for the nitrogen calculations although the same general trend is certainly maintained. In Figure 3 orbital energies obtained from the atomic SCF calculations are intercompared for arsenic, phosphorus, and nitrogen. A slope of 0.90 indicates a slightly lower theoretical chemical shift of arsenic as compared to phosphorus. The slope of 0.40 for arsenic *vs.* nitrogen shows the much greater chemical shift effects of the first-row atoms.

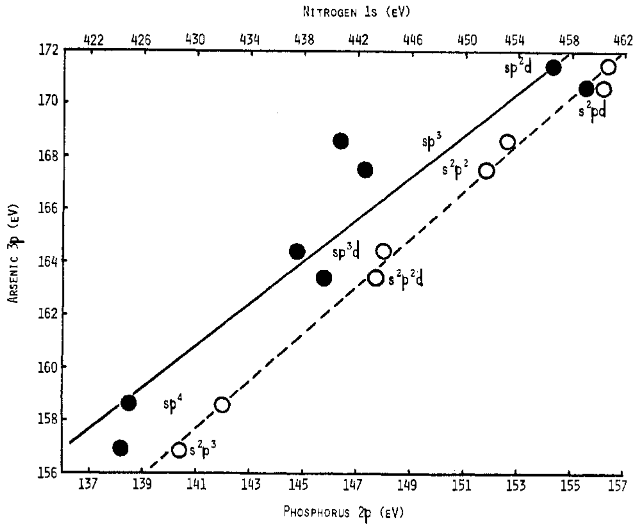

Figure 3.—A comparison of the arsenic 3p orbital energies and the phosphorus 2p and the nitrogen 1s orbital energies obtained from atomic SCF calculations. The orbital-energy shifts resulted from various valence electron configurations of the neutral atoms and their 1+ ions. The solid points and the solid line (slope 0.40) correspond to arsenic *vs.* nitrogen while the open points and the dotted line (slope 0.90) refer to arsenic *vs.* phosphorus. Both lines result from a least-squares treatment of the orbital energies presented in Table IV.

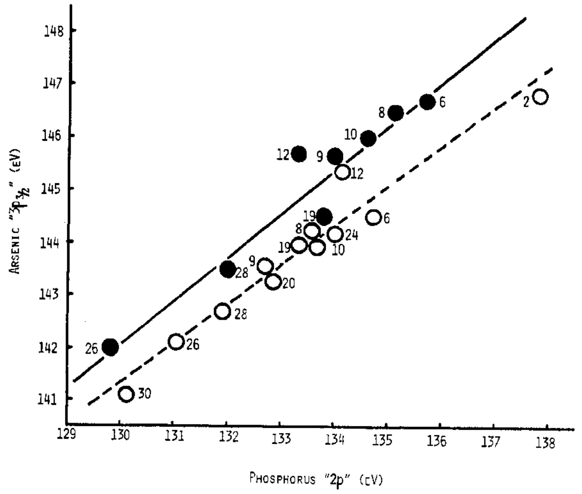

Figure 4.—The "$3p_{3/2}$" binding energies of arsenic *vs.* those of phosphorus "2p" for compounds having the same number, kind, and arrangement of substituent atoms. The numbering corresponds to the appropriate arsenic compounds in Table I. The solid points and the solid line (slope 0.83) correspond to directly measured (unreferenced) binding energies while the open points and the dotted line (slope 0.74) correspond to the residual hydrocarbon "1s" referenced measurements. Both lines result from a least-squares treatment of the data.

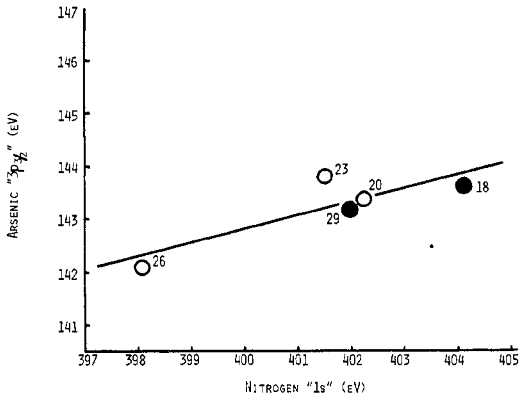

Figure 5.—The "$3p_{3/2}$" binding energies of arsenic *vs.* those of nitrogen "1s" for compounds which are similar in number, kind, and arrangement of substituent groups. The numbering corresponds to the appropriate arsenic compounds in Table I. The open points represent compounds which differ from the corresponding arsenic compounds by the interchange of alkyl for aryl groups. The straight line (slope 0.25) resulted from a least-squares treatment of the data.

Similarly, comparisons of the experimental chemical shifts are made in Figures 4 and 5. The comparison compounds utilized for these figures are numbered according to the corresponding arsenic compounds and are reported in Table V, along with their binding energies. Three of the nitrogen compounds are slightly different from their arsenic analogs because of interchange of alkyl for aryl groups; but this interchange has been shown to cause no distinguishable differences.[6] In Figure 4, the larger slope of the plot utilizing direct measurements reflects the effect of the reference material which tends to lower the larger binding energy values more than it does the smaller ones.

TABLE V

RELATED PHOSPHORUS AND NITROGEN MEASUREMENTS

No.[a]	Compd	Direct	Cor[b]
	P "2p"		
2	KPF_6	139.5	137.8
6	$Na_4P_2O_7$	135.7	134.7
			133.3[5]
8	Na_2HPO_4	135.1	133.6
9	Na_3PO_4	134.0	132.7
			132.1[5]
10	K_3PO_4	134.6	133.6
12	$(C_6H_5)PO(OH)_2$	133.3	134.1
19	$[(C_6H_5)_3PO]_2HgCl_2$	133.8	133.4
20	$(C_6H_5)_3PO$		132.8[6]
			132.7[5]
24	P_2S_5		134.0[5]
26	$(C_6H_5)_3P$	129.8	131.0
			131.3[6]
			130.6[5]
28	$[(C_6H_5)_3P]_2HgI_2$	132.0	131.9
			131.1[6]
30	P_{red}		130.1[5]
	N "1s"		
18	$NaNO_2$		404.1[2]
20	$(CH_3)_3NO$		402.2[3]
23	$(CH_3)_4NCl$		401.5[3]
26	$(C_4H_9)_3N$		398.1[3]
29	N_4S_4		402.1[2]

[a] The numbering corresponds to the analogous arsenic compounds in Table I. [b] Measurements referenced to hydrocarbon-contaminant "1s" line, assuming a value of 285.0 eV.

TABLE VI
RELATIVE CHEMICAL SHIFTS OF ANALOGOUS ARSENIC, PHOSPHORUS, AND NITROGEN CHEMICAL ENVIRONMENTS

Comparison	Source	Fig	Chem shift ratio,[c] arsenic: other atom
As "3p$_{3/2}$" *vs.* P "2p"	Exptl[a]	4	0.74
As "3p$_{3/2}$" *vs.* P "2p"	Exptl[b]	4	0.83
As 3p *vs.* P 2p	SCF	3	0.90
As "3d" *vs.* P "2p"	Exptl[a]		0.74
As "3d" *vs.* P "2p"	Exptl[b]		0.92
As 3d *vs.* P 2p	SCF		0.88
As "3p$_{3/2}$" *vs.* N "1s"	Exptl[a]	5	0.25
As 3p *vs.* N 1s	SCF	3	0.40
As "3d" *vs.* N "1s"	Exptl[a]		*Ca.* 0.34
As 3d *vs.* N 1s	SCF		0.39

[a] Binding energies corrected using hydrocarbon contaminant as reference material. [b] Directly measured binding energies. [c] Obtained from least-squares treatment of data.

The experimental values reflect the slightly smaller relative shift for arsenic compared to phosphorus and the much smaller shift for arsenic compared to nitrogen, in accord with the calculated values of Figure 3. A summation of the various chemical shift comparisons is presented in Table VI. This table shows that the variations in orbital energy from the SCF calculations on atoms parallel the experimental findings amazingly well. Note that the best fit between calculation and experiment is found for the direct (unreferenced) experimental data.

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Substituent Transmission Effects in Some Substituted Triphenylarsines and -stibines Using Nuclear Quadrupole Resonance Spectroscopy

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The arsenic, antimony, chlorine, and bromine nqr spectra for a number of ortho-, meta-, and para-substituted triphenylarsines and -stibines have been recorded. The substituents CH_3, CH_3O, CF_3, F, Cl, and Br were investigated along with $(C_6F_5)_3Sb$. There is a notable difference between the triarylarsines and -stibines. The correlation of the arsenic nqr data for the para substituents with Taft's resonance substituent constants suggests that arsenic–ring π interaction exists and is an efficient mechanism of substituent electronic transmission. In the stibine analogs correlation of the nqr data with Hammett's functions is good in all cases except for the CF_3 group. σ–π effects taken together appear more competitive in the stibines.

Introduction

Trivalent organometalloid compounds of group Va elements, P, As, Sb, and Bi all have a lone pair of electrons which is chemically important. The Lewis basicities of these elements toward metal ions as well as virtually all of their chemical reactions involve this lone pair. Triphenylarsine, -stibine, and -bismuthine lack the basic character of their trialkyl analogs, which suggests some delocalization of the lone pair onto the ring.[1] Arguments both for[2] and against[3] this type of delocalization have been presented based on the uv spectra of the arsine and stibine. These data, however, reflect excited-state effects and may not be directly applicable to the ground state.

There is some evidence that the set of substituent parameters to which experimental data correlate is indicative of the mechanism of transmission of substituent character to a point of observation.[4] Additional information regarding the nature of pnigogen atom–aryl bonding could possibly be revealed in the arsenic and antimony nqr spectra in substituted aryl systems. Correlation of the ^{75}As and ^{121,123}Sb nqr data with the resonance substituent parameters of Taft, *et al.*,[5] would suggest a definite amount of ring–lone pair interaction. Correlation of data with the more general substitutent constants of Hammett[6] suggests that nqr coupling is sensitive to competitive inductive effects in the σ framework of the molecule and the π resonance effects.

Experimental Section

Syntheses.—The syntheses and properties of most of the compounds mentioned in this study have been previously reported and are summarized in Table I. The triphenylstibine, purchased from M and T Chemicals, Inc., Rahway, N. J., was recrystallized from ethanol. The other compounds were made by one of the following two general methods as described in previous preparations of these compounds: (A) reaction of an aryl Grignard reagent with either $AsCl_3$ or $SbCl_3$; (B) the reac-

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