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AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF CHARGE DISTRIBUTIONS IN TETRACOVALENT COMPOUNDS OF NITROGEN AND PHOSPHORUS

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An X-Ray Photoelectron Spectroscopic Study of Charge Distributions in Tetracovalent Compounds of Nitrogen and Phosphorus

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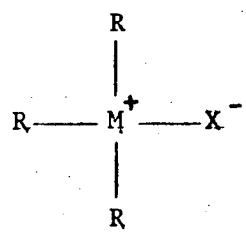
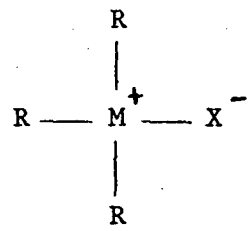
Abstract: Core electron binding energies for ten phosphorus and four nitrogen compounds have been measured by X-ray photoelectron spectroscopy in the gas phase. The chemical shifts have been correlated by the electrostatic potential equation using charge distributions from extended Hückel theory and CNDO/2 molecular orbital calculations. The data indicate that resonance structures of the type



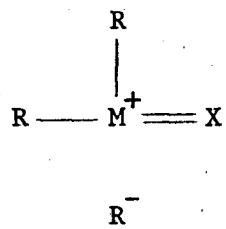
contribute significantly to the charge distributions in the tetracovalent compounds. The data for the phosphorus compounds can be quantitatively rationalized without the inclusion of any $p\pi \rightarrow d\pi$ bonding between the central atom and the X ligand, but the effects of electronic relaxation upon the core binding energy chemical shifts must be included.

Introduction

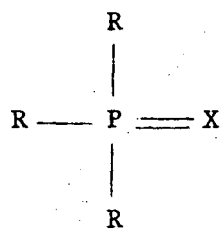
The bonding in four-coordinate compounds of nitrogen and phosphorus can be represented by the following type of valence-bond structure.



However, because these compounds generally have short M-X bond lengths and high M-X stretching frequencies, multiple bond character has been postulated for the M-X bonds. Such multiple bonding can be explained by hyperconjugation, i.e., no-bond resonance:[1,2]



When the central atom is phosphorus, however, it is conceivable that the phosphorus 3d orbitals may significantly participate in the bonding.[2-4] In this case, a resonance structure having no formal charges, such as the following, would be appropriate.



The latter structure implies $p\pi \rightarrow d\pi$ bonding between the central phosphorus atom and the peripheral X ligand.

To help resolve the question of the bonding in these compounds, we have measured the core binding energies, by means of X-ray photoelectron spectroscopy,[5] of the following tetracovalent compounds: $N(CH_3)_3BH_3$, $N(CH_3)_3O$, $P(CH_3)_3BH_3$, $P(CH_3)_3CH_2$, $P(CH_3)_3NH$, $P(CH_3)_3O$, $P(CH_3)_3S$, $POCl_3$, and $PSCl_3$. We have also measured binding energies for the simpler compounds $N(CH_3)_3$, $P(CH_3)_3$, PCl_3, NH_3 and PH_3. These binding energies were measured for gas-phase samples and represent true molecular ionization potentials, free from solid-state effects such as sample charging, contact potentials, and lattice potentials. We have interpreted the chemical shifts qualitatively using simple electronegativity concepts and quantitatively using results from extended Hückel theory[6] (EHT) and CNDO/2[7] molecular orbital calculations.

Experimental Section

Anhydrous NH_3 and $N(CH_3)_3$ were obtained from the Matheson Company and were used as received. PCl_3 was obtained from the Mallinckrodt Chemical Works; $POCl_3$ was obtained from the Matheson, Coleman, and Bell Company; $PSCl_3$ was obtained from the Research Organic/Inorganic Chemical Corporation. All three were distilled under dry nitrogen, and their boiling points (76°, 106°, and 123°, respectively) agreed with literature values.[8] Trimethylamine-N-oxide dihydrate was obtained from the Eastman Kodak Company and dehydrated by distillation with dimethylsulfoxide followed by vacuum sublimation; the melting point (96°-98°) of the product agreed with the literature value[8] for the anhydrous form of trimethylamine-N-oxide. Trimethylamine borane from the Callery Chemical Company was used as received. Phosphine was prepared from hypophosphorous acid;[9] its vapor pressure (170 torr at -111°) agreed with the literature.[9]

Trimethylphosphine sulfide was prepared from $P(CH_3)_3 \cdot HgCl$ and ammonium polysulfide;[10] its melting point (152-153°) agreed with the literature.[10] The sources of the other compounds have been described in a previous publication.[11]

All spectra were obtained for samples in the gas phase using the Berkeley iron-free, double-focusing magnetic spectrometer.[12] Gaseous samples and the vapors of liquid and volatile solid samples were leaked into the irradiation chamber together with argon gas. Sample pressure and argon pressure in the irradiation chamber were approximately 40-50μ and 20-30μ, respectively. Less volatile solid samples were placed directly inside the irradiation chamber, which resembles an effusion cell, and spectra were taken of the vapors over the solids. Argon was simultaneously leaked into the irradiation chamber to maintain a pressure of about 10μ. The spectra were taken using magnesium Kα radiation. Core levels of the samples and the reference gas, argon, were alternately scanned.

The spectra were fit by a least-squares analysis to Lorentzian lineshapes using a computer program described by Fadley.[13] The absolute ionization potentials were calculated on the basis of 248.45 eV for the $2p_{3/2}$ level in argon. The reproducibility of the data was determined for several compounds to be about ±0.05 eV. We were unable to measure the N 1s level in $N(CH_3)_3O$ in several attempts, despite being able to measure the C 1s and O 1s levels. To ensure that the vapor from the solid was indeed $N(CH_3)_3O$, the sample was removed from the ESCA spectrometer and analyzed by mass spectroscopy. The mass spectrum showed a strong parent peak for $N(CH_3)_3O^+$ at m/e = 75 and peaks corresponding to the loss of methyl groups at m/e = 60, 45, and 30. We believe that the N 1s spectrum

was obscured by noise.

Experimental values of molecular geometries and internuclear distances, which were used in the molecular orbital calculations and potential correlations, were taken from the literature[14-18] whenever possible. In a few cases, where accurate geometries were not available, values were estimated from data for similar compounds.

Binding Energy Correlations

ESCA chemical shifts are due to the changes in the coulombic potential felt at a core electron shell in atoms in different chemical environments.[5] To a very rough approximation, changes in core binding energy for a given element are linearly related to changes in the charge of the atom. That is,

$$E_B(A) = kQ_A + \ell \qquad (1)$$

where k and ℓ are parameters. A more sophisticated model, the point charge potential equation[5] involves the relation

$$E_B(A) = kQ_A + \sum_{B \neq A} Q_B/R_{AB} + \ell \qquad (2)$$

This model includes the potential due to the other atoms in the molecule, which are treated as point charges separated from the ionized atom by the internuclear distances. As before, k and ℓ are parameters, usually evaluated by a least-squares fit of the charges to the binding energies. The parameter k may be interpreted[19] as the average $\langle r^{-1} \rangle$ expectation value for the valence orbitals on atom A, and ℓ represents the binding energy of a free atom of A.

If the charge distribution of a molecule is determined from a molecular orbital calculation, the quantum mechanical potential at atom A can be calculated from the density matrix and the appropriate r^{-1} integrals. A simpler approach, which is especially applicable to semi-empirical MO calculation, uses a valence potential first proposed by Schwartz[19,20] where:

$$\Phi_{val} = -\sum_{i \in A} P_i \langle r^{-1} \rangle_i + \sum_{B \neq A} Q_B / R_{AB} \qquad (3)$$

Here P_i is the gross population in the ith valence orbital and Q_B is the net charge on atom B, both determined by Mulliken population analysis. Equation 3 is similar to equation 2, except that the one-center $\langle r^{-1} \rangle$ integrals are calculated from wavefunctions rather than evaluated empirically. Using equation 3 to evaluate $\Phi_{val}(A)$, the binding energies are calculated from the relation

$$E_B(A) = c\Phi_{val}(A) + \ell \qquad (4)$$

where c is an adjustable parameter which helps to compensate for the approximate nature of most semi-empirical MO theories and ℓ now represents the binding energy for a hypothetical atom stripped of all valence electrons.

In the preceding discussion, we have assumed that chemical shifts may be interpreted in terms of ground-state charge distributions. However, during photoionization, the remaining electrons in the molecule are attracted toward the core hole. Although the electronic relaxation produces a large change in the coulombic potential, this change is nearly the same for similar molecules, thus allowing the use of ground-state

charge distributions. A more appropriate "transition state" may, however, be approximated in the valence potential model, equation 4, by using a result of Hedin and Johansson[21] together with the principle of equivalent cores.[22] The hole state binding energy may be expressed[23] as:

$$E_B(A) = c \times \tfrac{1}{2}[\Phi_{val}(A) + \Phi_{val}(B^+)] + \ell \qquad (5)$$

where $\Phi_{val}(B^+)$ is the potential calculated for the isoelectronic cation obtained by substituting the core of atom A with the core of atom B, the next element in the periodic table.

Results and Discussion

Core binding energies for the nitrogen compounds are given in Table I. Similar data for the phosphorus compounds appear in Table II. The order of these binding energies can be almost exactly predicted using two simple notions: that, for a given element, the charge on an atom is approximately linearly related to the sum of the Pauling electronegativities of the other atoms to which the atom is bonded, and that the core binding energy is linearly related to charge. On this basis, the nitrogen binding energies should be ordered:

$$NH_3 < N(CH_3)_3 < N(CH_3)_3BH_3$$

For the phosphorus series, the order should be:

$$PH_3 < P(CH_3)_3 < PCl_3 < P(CH_3)_3BH_3 < P(CH_3)_3CH_2 \approx P(CH_3)_3S$$

$$< P(CH_3)_3NH < P(CH_3)_3O < PSCl_3 < POCl_3$$

Except for the misplacements of NH_3, PH_3 and PCl_3, these orders were observed experimentally. In the following sections, we discuss more sophisticated, quantitative methods for correlating the chemical shifts.

Table I

Experimental Core Binding Energies for Some Compounds of Nitrogen (in eV)

Compound	E_B(N 1s)[a]	E_B(C 1s)[a]	E_B(X)[a,b]
NH_3	405.43	---	---
$N(CH_3)_3$	404.63	291.09	---
$N(CH_3)_3BH_3$	406.51	291.80	193.20
$N(CH_3)_3O$	---	291.60	537.5
$P(CH_3)_3NH$	402.38	290.63	---

[a] The uncertainty in the experimental values is approximately ±0.05 eV, except for ±0.1 eV in the O 1s binding energy of $N(CH_3)_3O$.

[b] The binding energies are for the B 1s and O 1s levels.

Table II

Experimental Core Binding Energies for Some Compounds of Phosphorus (in eV)

Compound	$E_B(P\ 2p_{3/2})^a$	$E_B(R)^{a,b}$	$E_B(X)^{a,c}$
PH_3	136.87	---	---
$P(CH_3)_3$	135.76	290.13	---
$P(CH_3)_3BH_3$	137.00	290.79	192.76
$P(CH_3)_3CH_2$	137.03	290.40	287.83
$P(CH_3)_3NH$	137.39	290.63	402.38
$P(CH_3)_3O$	137.63	290.57	535.88
$P(CH_3)_3S$	137.45	290.60	166.91
PCl_3	139.60	206.27	---
$POCl_3$	140.87	207.16	537.80
$PSCl_3$	140.45	206.71	168.70

[a] The uncertainty in the experimental values is approximately ±0.05 eV.

[b] The first six entered binding energies are for the C 1s level in the methyl groups; the last three binding energies are for the Cl $2p_{3/2}$ level.

[c] The binding energies are for the B 1s, C 1s, N 1s, O 1s, S $2p_{3/2}$, O 1s and S $2p_{3/2}$ levels.

EHT Correlations. The valence potential model, equation 4, was used to correlate binding energies with EHT charge distributions. The original formulation of the EHT method by Hoffmann[6] was used for these calculations. The ionization energies and wavefunctions used in our program have been described previously.[24] A valence, s, p basis set was used for all the atoms except hydrogen (an s basis set) and phosphorus (for which valence d orbitals were also included). The calculated valence potentials are given in Table III. This table also includes the parameters c and ℓ for each element and, when more than two binding energies for a given element were correlated, the standard deviation and correlation coefficient. The correlations of the carbon, nitrogen, and phosphorus binding energies involve enough data to warrant individual discussion.

The high correlation coefficients obtained for the carbon 1s and nitrogen 1s binding energies show that, to a good approximation, the EHT ground-state potentials are linearly related to the binding energies. The values of c (0.185 and 0.205 for carbon and nitrogen, respectively) are much smaller than unity and indicate that EHT-calculated charge separations are exaggerated. A plot of calculated vs experimental binding energies for the carbon 1s data is shown in Fig. 1. It can be seen that the binding energy of the CH_2 carbon in $P(CH_3)_3CH_2$ is very low, as would be expected from its negative formal charge.

The correlation coefficient of the phosphorus $2p_{3/2}$ binding energies and the EHT potentials is relatively low, and the corresponding plot, in Fig. 2, shows considerable scatter. The phosphorus compounds appear to fall into three groups: the six trimethyl compounds, the three

Table III

Ground State Valence Potentials[a] from EHT Calculations and Data from the Correlations of Core Binding Energies with EHT Potentials

Compound	$\Phi_{val}(P)$	Dev.(P)[b]	$\Phi_{val}(N)$	Dev.(N)[b]	$\Phi_{val}(C)$	Dev.(C)[b]	$\Phi_{val}(B)$	$\Phi_{val}(O)$	$\Phi_{val}(S)$	$\Phi_{val}(Cl)$
NH_3	---	---	153.68	0.09	---	---	---	---	---	---
$N(CH_3)_3$	---	---	157.22	-0.01	91.60	0.12	---	---	---	---
$N(CH_3)_3BH_3$	---	---	147.59	-0.07	89.65	0.45	55.98	---	---	---
$N(CH_3)_3O$	---	---	131.37	c	87.48	-0.13	---	222.55	---	---
PH_3	74.83	1.10	---	---	---	---	---	---	---	---
$P(CH_3)_3$	72.94	-0.45	---	---	95.81	0.0	---	---	---	---
$P(CH_3)_3BH_3$	65.48	-0.94	---	---	93.24	0.10	58.09	---	---	---
$P(CH_3)_3CH_2$	65.39	-0.93	---	---	93.36	-0.27	---	---	---	---
	---	---	---	---	108.97	0.05	---	---	---	---
$P(CH_3)_3NH$	64.41	-0.80	168.04	-0.03	93.00	-0.10	---	---	---	---
$P(CH_3)_3O$	62.55	-0.99	---	---	92.40	-0.24	---	227.39	---	---
$P(CH_3)_3S$	63.34	-0.99	---	---	93.75	-0.03	---	---	107.66	---
PCl_3	66.51	1.89	---	---	---	---	---	---	---	135.54
$POCl_3$	58.74	1.36	---	---	---	---	---	224.01	---	131.57
$PSCl_3$	57.96	0.76	---	---	---	---	---	---	108.60	132.06
c	0.232		0.204		0.185		0.209	0.376	-1.904	0.188
ℓ	153.16		436.66		307.90		204.87	621.45	-38.10	231.73
Std. Dev.	1.15		0.07		0.21		---	0.44	---	0.18
Corr. Coeff.	0.737		0.999		0.981		---	0.903	---	0.914

[a] All potentials are negative and in eV.

[b] $Dev(X) = E_B(X) - [c_X\Phi_{val}(S) + \ell_X]$(eV).

[c] This binding energy was not measured.

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trichloro compounds, and phosphine. The two dashed lines in Fig. 2 represent separate correlations for the trimethyl and trichloro compounds. The parameters for these lines are, for the trimethyl compounds, c = 0.179, std. dev. = 0.07 eV, corr. coeff. = 0.994, and for the trichloro compounds, c = 0.125, std. dev. = 0.260 eV, corr. coeff. = 0.916. These parameters indicate much better correlations than obtained for all the data, and suggest that, although the EHT calculations can give meaningful relative charge distributions for a fairly homogeneous series of molecules, the method is less useful in quantitatively predicting changes in markedly different molecules.

EHT transition state potentials for phosphorus were calculated using Eq. 5; the data are listed in Table IV. A slight improvement in the correlation was obtained by this method. If the transition state potentials for the six trimethyl and the three trichloro compounds are correlated separately, better fits are obtained than with the ground state potentials. The transition state correlations give the following results: for the trimethyl compounds, c = 0.168, std. dev. = 0.05 eV, corr. coeff. = 0.998, and, for the trichloro compounds, c = 0.126, std. dev. = 0.21 eV, corr. coeff. = 0.994. Thus, the inclusion of even crudely estimated relaxation effects improves the correlations.

Although phosphorus valence d orbitals were included in the EHT basis sets, they had little effect on the composition of the filled molecular orbitals and hence on the calculated charge distributions. The good correlation of EHT potentials with the P $2p_{3/2}$ binding energies

of the organophosphorus compounds may be interpreted either as showing a constant amount of d orbital bonding in that series or as showing that such bonding is unimportant, at least in determining charge distributions.

CNDO/2 Correlations. The valence potential model was also used to correlate binding energies with CNDO/2 charge distributions. For atoms lighter than neon, the procedures and parameters described by Pople and Beveridge[7] were followed. Two sets of parameters for the second row elements were used - those proposed by Santry and Segal,[25] included in the Pople and Beveridge book,[7] and those which we previously used for calculations involving second and third row elements.[24] The latter parameters are based on orbital ionization potentials and electron affinities determined by Hinze and Jaffé[26,27] and Slater s orbital wavefunctions porposed by Cusachs and Corrington.[28] Values of β_o were estimated using the method of Santry and Segal.[25] In the s,p,d calculations using the Hinze-Jaffé parameters, the quantity $\frac{1}{2}(I_d + A_d)$ was simply set to zero for P, S, and Cl.

Four sets of correlations of binding energies with CNDO/2 ground-state valence potentials were made. Potentials for the first set were calculated using an s,p,d, basis set and Santry-Segal parameters for second-row atoms. Potentials for the second set of correlations also included s,p,d basis sets for second row elements, but used the Hinze-Jaffé-based parameters. Potentials for the third set were calculated using Santry-Segal parameters and s,p basis sets; potentials for the fourth set were calculated using the Hinze-Jaffé based parameters and s,p basis

Table IV

Hole State Valence Potentials[a] for Phosphorus from EHT Calculations and Data from the Correlation of Phosphorus Binding Energies with the EHT Potentials

Compound	$\Phi_{val}(P)$	Dev(P)[b]
PH_3	80.66	1.07
$P(CH_3)_3$	79.51	-0.31
$P(CH_3)_3BH_3$	72.26	-0.76
$P(CH_3)_3CH_2$	71.70	-0.86
$P(CH_3)_3NH$	70.29	-0.83
$P(CH_3)_3O$	68.18	-1.09
$P(CH_3)_3S$	69.65	-0.92
PCl_3	72.26	1.84
$POCl_3$	63.88	1.15
$PSCl_3$	63.83	0.72
c_P	0.234	
ℓ_P	154.64	
Std. Dev.	1.08	
Corr. Coeff.	0.770	

[a] All potentials are negative and in eV.

[b] $Dev(P) = E_B(P\ 2p_{3/2}) - [k_P\Phi_{val}(P) + \ell_P](eV)$.

sets. As measured by the correlation coefficients and standard deviations, the correlations using s,p,d potentials were worse than the correlations using s,p potentials, and we conclude that the valence d orbitals of phosphorus are not important in determining the charge distributions of these compounds.

The third and fourth sets of ground-state correlations, involving s,p potentials, were of comparable quality. In Table V we present the data for the calculations using the Hinze-Jaffé parameters. We also made calculations with s,p basis sets and both types of parameters for transition-state potentials, using eq. 5. These transition-state potentials, which should better represent the charge distributions corresponding to the chemical shifts, did in fact improve the correlations for the carbon, nitrogen, and phosphorus binding energies, the three series for which we have a meaningful number of data. Again the quality of the correlations for the two sets of parameters were comparable, but the transition state s,p potentials using the Hinze-Jaffé-based parameters gave better correlations. Data for the latter calculations are given in Table VI.

The values of the parameter c_C for the ground-state binding energy correlation, 0.386, and for the transition-state correlation, 0.499, are larger than the value for c_C from the EHT correlation, indicating that the CNDO/2 charge distributions are, as expected, less polarized than EHT charge distributions. However, even for the transition-state correlation, c_C is considerably less than one. This result is difficult to explain since

other carbon binding energy correlations using CNDO/2 potentials have given values of c_C much nearer to unity, the theoretical value.[19,20] In the transition-state correlations for carbon, illustrated in Fig. 3, the points for both the nitrogen and phosphorus compounds fit a single line very well, whereas, in a corresponding plot of the ground-state data the carbon points representing $N(CH_3)_3$, $N(CH_3)_3BH_3$, and $N(CH_3)_3O$ all are appreciably above the least-squares line. This observation suggests that there is a greater amount of electronic relaxation in the ionization of a methyl carbon atom in a phosphorus compound than in the corresponding nitrogen compound. In other words, PR_2 and PR_2X are more electronically polarizable groups than are NR_2 and NR_2X.

The c_N values parallel the c_C values. For the ground-state correlation c_N equals 0.382, while for the transition-state correlation c_N equals 0.439. A comparison of the ground-state and transition-state correlations discloses a typical failing of ground-state correlations. For ground-state potentials, $\Phi_{val}(\underline{N}H_3) < \Phi_{val}\underline{N}(CH_3)_3$, whereas $E_B(\underline{N}H_3) > E_B\underline{N}(CH_3)_3$. The transition-state potentials, however, do show the correct order: $\Phi_{val}(\underline{N}H_3) > \Phi_{val}\underline{N}(CH_3)_3$. The results indicate that there is greater electronic relaxation of a CH_3 group adjacent to an atom undergoing photoemission than of an H atom adjacent to an atom undergoing photoemission.

The c_P values, 0.681 for the ground-state potentials and 0.782 for the transition-state potentials, are somewhat larger than the corresponding values of c_C and c_N. As was also the case for the

Table V

Ground State Valence Potentials[a] from CNDO/2 Calculations and Data from the Correlation of Core Binding Energies with CNDO/2 Potentials

Compound	$\Phi_{val}(P)$	Dev(P)[b]	$\Phi_{val}(N)$	Dev(N)[b]	$\Phi_{val}(C)$	Dev(C)[b]	$\Phi_{val}(B)$	$\Phi_{val}(O)$	$\Phi_{val}(S)$	$\Phi_{val}(Cl)$
NH_3	---	---	135.66	0.75	---	---	---	---	---	---
$N(CH_3)_3$	---	---	134.63	-0.44	87.84	0.47	---	---	---	---
$N(CH_3)_3BH_3$	---	---	130.55	-0.12	86.17	0.52	56.85	---	---	---
$N(CH_3)_3O$	---	---	130.20	c	86.66	0.53	---	197.28	---	---
PH_3	82.98	0.92	---	---	---	---	---	---	---	---
$P(CH_3)_3$	82.96	-0.21	---	---	88.34	-0.22	---	---	---	---
$P(CH_3)_3BH_3$	80.60	-0.57	---	---	87.04	-0.16	56.97	---	---	---
$P(CH_3)_3CH_2$	80.42	-0.67	---	---	87.51	-0.36	---	---	---	---
	---	---	---	---	95.31	0.08	---	---	---	---
$P(CH_3)_3NH$	80.54	-0.22	141.16	-0.19	86.64	-0.47	---	---	---	---
$P(CH_3)_3O$	80.84	0.22	---	---	87.67	-0.10	---	195.39	---	---
$P(CH_3)_3S$	79.87	-0.68	---	---	87.15	-0.28	---	---	117.14	---
PCl_3	79.10	1.00	---	---	---	---	---	---	---	143.11
$POCl_3$	76.26	0.34	---	---	---	---	---	191.84	---	142.31
$PSCl_3$	76.19	-0.13	---	---	---	---	---	---	114.11	141.74
c	0.681		0.382		0.386		3.667	0.118	0.591	0.372
ℓ	192.44		456.54		324.49		401.65	559.99	236.11	259.74
Std. Dev.	0.61		0.52		0.38		---	0.98	---	0.36
Corr. Coeff.	0.933		0.955		0.936		---	0.315	---	0.576

[a] All potentials are negative and in eV.

[b] $Dev(X) = E_B(X) - [c_X\Phi_{val}(X) + \ell_X]$(eV).

[c] This binding energy was not measured.

Table VI

Transition State Valence Potentials[a] from CNDO/2 Calculations and Cata from the Correlation of Core Binding energies with CNDO/2 Potentials

Compound	$\Phi_{val}(P)$	Dev(P)[b]	$\Phi_{val}(N)$	Dev(N)[b]	$\Phi_{val}(C)$	Dev(C)[b]	$\Phi_{val}(B)$	$\Phi_{val}(O)$	$\Phi_{val}(S)$
NH_3	---	---	154.39	-0.13	---	---	---	---	---
$N(CH_3)_3$	---	---	156.11	-0.18	104.99	-0.03	---	---	---
$N(CH_3)_3BH_3$	---	---	152.74	0.22	103.59	-0.04	68.63	---	---
$N(CH_3)_3O$	---	---	152.34	c	104.13	0.05	---	---	---
PH_3	91.23	-0.12	---	---	---	---	---	220.04	---
$P(CH_3)_3$	92.85	0.04	---	---	106.53	-0.15	---	---	---
$P(CH_3)_3BH_3$	90.88	-0.26	---	---	105.49	-0.10	69.22	---	---
$P(CH_3)_3CH_2$	90.63	-0.43	---	---	106.98	0.25	---	---	---
	---	---	---	---	111.52	-0.05	---	---	---
$P(CH_3)_3NH$	90.74	0.02	161.84	0.09	106.15	0.07	---	---	---
$P(CH_3)_3O$	91.00	0.46	---	---	d	---	---	220.33	---
$P(CH_3)_3S$	90.12	-0.41	---	---	106.03	0.00	---	---	127.02
PCl_3	89.13	0.97	---	---	---	---	---	---	---
$POCl_3$	86.22	0.04	---	---	---	---	---	216.70	---
$PSCl_3$	86.51	-0.23	---	---	---	---	---	---	124.19
c	0.782		0.439		0.499		0.746	0.346	0.633
ℓ	208.36		473.41		341.50		244.38	612.78	247.25
Std. Dev.	0.43		0.19		0.13		---	0.76	---
Corr. Coeff.	0.968		0.994		0.993		---	0.675	---

[a] All potentials are negative and in eV.

[b] $Dev(X) = E_B(X) - [c_X\Phi_{val}(X) + \ell_X]$(eV).

[c] This binding energy was not measured.

[d] The equivalent core calculation for this hole state potential did not achieve self consistency.

CNDO/2 carbon and nitrogen binding energy correlations, the transition-state correlation for the phosphorus binding energies is appreciably better than the ground-state correlation. Again, the most dramatic improvement was obtained for the hydride, in this case PH_3. The ground-state potentials predict the order $\Phi_{val}(\underline{P}H_3) < \Phi_{val}[\underline{P}(CH_3)_3] < \Phi_{val}[\underline{P}(CH_3)_3BH_3]$, whereas $E_B[\underline{P}(CH_3)_3] < E_B(\underline{P}H_3) < E_B[\underline{P}(CH_3)_3BH_3]$. When the transition-state potentials are considered, however, both the direction and the magnitude of the shifts are accounted for. Thus essentially the entire 1 eV shift in binding energy between PH_3 and $P(CH_3)_3$ is due to the changes in the potentials upon photoemission and not to differences between the ground-state potentials.

Because the difference between the ground-state and transition-state potentials for a given molecule is principally due to valence electrons relaxing toward the positively charged ionized core, one expects that the difference between these potentials, that is the <u>valence relaxation energy</u> for that molecule, should depend upon the number of ligands bonded to the core ionized atom, and upon the polarizabilities of these ligands. We previously found in a study of germanium compounds[29] that Cl and CH_3 groups have similar valence relaxation energies, larger than that of H. In the case of the trivalent phosphorus compounds, $\Phi_{val}(\underline{P}Cl_3) - \Phi_{val}[\underline{P}(CH_3)_3]$ has about the same value for ground-state potentials ($\Delta\Phi_{val} \simeq 3.9$ eV) as for transition-state potentials ($\Delta\Phi_{val} \simeq 3.7$ eV). However, $\Phi_{val}(\underline{P}Cl_3) - \Phi_{val}(\underline{P}H_3)$ has a value for ground-state potentials ($\Delta\Phi_{val} = 3.9$ eV) which is more than 1 eV greater than the value for transition-state potentials ($\Delta\Phi_{val} = 2.1$ eV).

This difference is caused by the greater polarizability of Cl relative to H. A tetracovalent molecule $P(CH_3)_3X$ ought to have a larger valence relaxation energy than trivalent $P(CH_3)_3$. In accord with this prediction, the difference $\Phi_{val}[\underline{P}(CH_3)_3NH] - \Phi_{val}[\underline{P}(CH_3)_3]$ for the ground-state potentials is 2.4 eV, whereas for transition-state potentials it is 2.1 eV.

The binding energy correlations for boron, oxygen, sulfur, and chlorine have too few data points to justify detailed analysis. In the ground state correlations of these elements, the parameter c varies from 0.118 to 3.667. These extreme values indicate that the ground-state potentials poorly describe the chemical shifts. The c values from the transition-state correlations, which range from 0.346 to 0.746, are closer to those of the carbon, nitrogen, and phosphorus correlations. Thus, it again appears necessary to consider the transition-state potentials to quantitatively interpret chemical shifts.

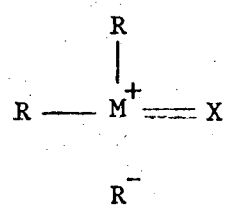
Conclusions

Simple Lewis valence bond structures for these tetracovalent Group V compounds suggest that the central atoms have a high positive charge while the peripheral BH_3, CH_2, NH, O, or S ligands have a high negative charge. Our data support this idea. The central atom binding energies of all the tetracovalent compounds are higher than the binding energies for the corresponding trivalent compounds, and the binding energies of the ligand atoms which have negative formal charges are unusually low for those elements.

Although direct evidence for or against the presence of multiple bonding in these compounds was not obtained by the methods discussed in

this paper, certain conclusions may be inferred from our data. If the phosphorus 3d orbitals of the phosphorus compounds participate in $p\pi \rightarrow d\pi$ bonding, these interactions would be expected to increase the electron density of the phosphorus atoms at the expense of the formally-charged peripheral atoms, X. Because we were able to obtain good correlations of the core binding energies of phosphorus and the X atoms by three different methods, all of which neglected or minimized $p\pi \rightarrow d\pi$ interactions, the following conclusion seems reasonable. Either the d orbitals are of comparable importance in determining the charge distributions of all the phosphorus compounds, including PH_3, $P(CH_3)_3$, and PCl_3, or they do not significantly affect the charge distributions of any of the compounds studied. We believe the latter hypothesis is correct. Certain specific data also directly argue against d orbital bonding. The B 1s and O 1s binding energies of the compounds $M(CH_3)_3BH_3$ and $M(CH_3)_3O$ are lower when M = P than when M = N. This result strongly suggests a greater negative charge on the BH_3 and O ligands for the phosphorus compounds than for the nitrogen compounds, in agreement with simple electronegativity predictions. This behavior is inconsistent with the presence of appreciable $p\pi \rightarrow d\pi$ bonding in the phosphorus compounds.

Multiple bonding between the central atom and a ligand atom is still possible for both the phosphorus and nitrogen compounds if one considers no-bond hyperconjugated resonance structures such as the following:



We have elsewhere[11] interpreted core binding energy data in terms of such bonding. In this type of bonding, charge is not transferred from the X ligand to the central atom as in $p\pi \rightarrow d\pi$ bonding, but rather charge is transferred from the X ligand to the other peripheral ligands. Although bond order is not a particularly well-defined concept in molecular orbital descriptions of chemical bonding, we have carefully examined the EHT and CNDO/2 calculations for $POCl_3$ and $PSCl_3$ in order to infer bond orders for these molecules. The EHT Mulliken population analyses show little π electron density in the P-O and P-S overlap regions, and the $p\pi$ orbitals on oxygen and sulfur are nearly filled and exhibit primarily lone-pair characteristics. Although there are no overlap populations in CNDO/2, the $p\pi$ orbitals of oxygen and sulfur are again nearly filled, and an examination of the eigenvectors for the filled molecular orbitals again suggests that these orbitals are largely lone pairs. Thus, simple molecular orbital descriptions of the ground states of these two molecules show primarily σ bonding and considerable charge polarization. However, more sophisticated calculations should be made if the importance of hyperconjugation in these molecules is to be theoretically determined. The calculation of localized molecular orbitals might be especially helpful in determining the extent of hyperconjugation.

Our best correlations of binding energies with charge distributions were obtained when the effect of electronic relaxation due to the core hole was explicitly included in the charge distributions. We feel that the effects of electronic relaxation during photoemission on core binding energies will become more apparent as more gas phase core binding energies

for compounds containing elements heavier than neon are measured. These heavier atoms are generally more polarizable than first row atoms, and therefore are more perturbed by positively charged holes in either their own cores, or the cores of adjacent atoms. Furthermore, the increased size of these heavier elements implies smaller one-center $\langle r^{-1} \rangle$ expectation values and thus smaller chemical shifts. Thus, the effects of valence electron relaxation should become relatively more pronounced. The equivalent cores approach, in both its thermodynamic[22] and electrostatic potential[23] applications, provides a simple method of accounting for the valence electron charge polarization which occurs during photoemission.

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Figure Captions

Fig. 1. Plot of carbon 1s binding energies vs binding energies calculated from ground state EHT valence potentials, where $E_B(\text{calc}) = c\Phi + \ell$.

Fig. 2. Plot of phosphorus $2p_{3/2}$ binding energies vs binding energies calculated from ground state EHT valence potentials, where $E_B(\text{calc}) = c\Phi + \ell$. The two dashed lines represent correlations of just the trimethyl and just the trichloro compounds.

Fig. 3. Plot of carbon 1s binding energies vs binding energies calculated from hole state CNDO/2 valence potentials, where $E_B(\text{calc}) = c\Phi + \ell$.

Fig. 4. Plot of phosphorus $2p_{3/2}$ binding energies vs binding energies calculated from hole state CNDO/2 valence potentials, where $E_B(\text{calc}) = c\Phi + \ell$.

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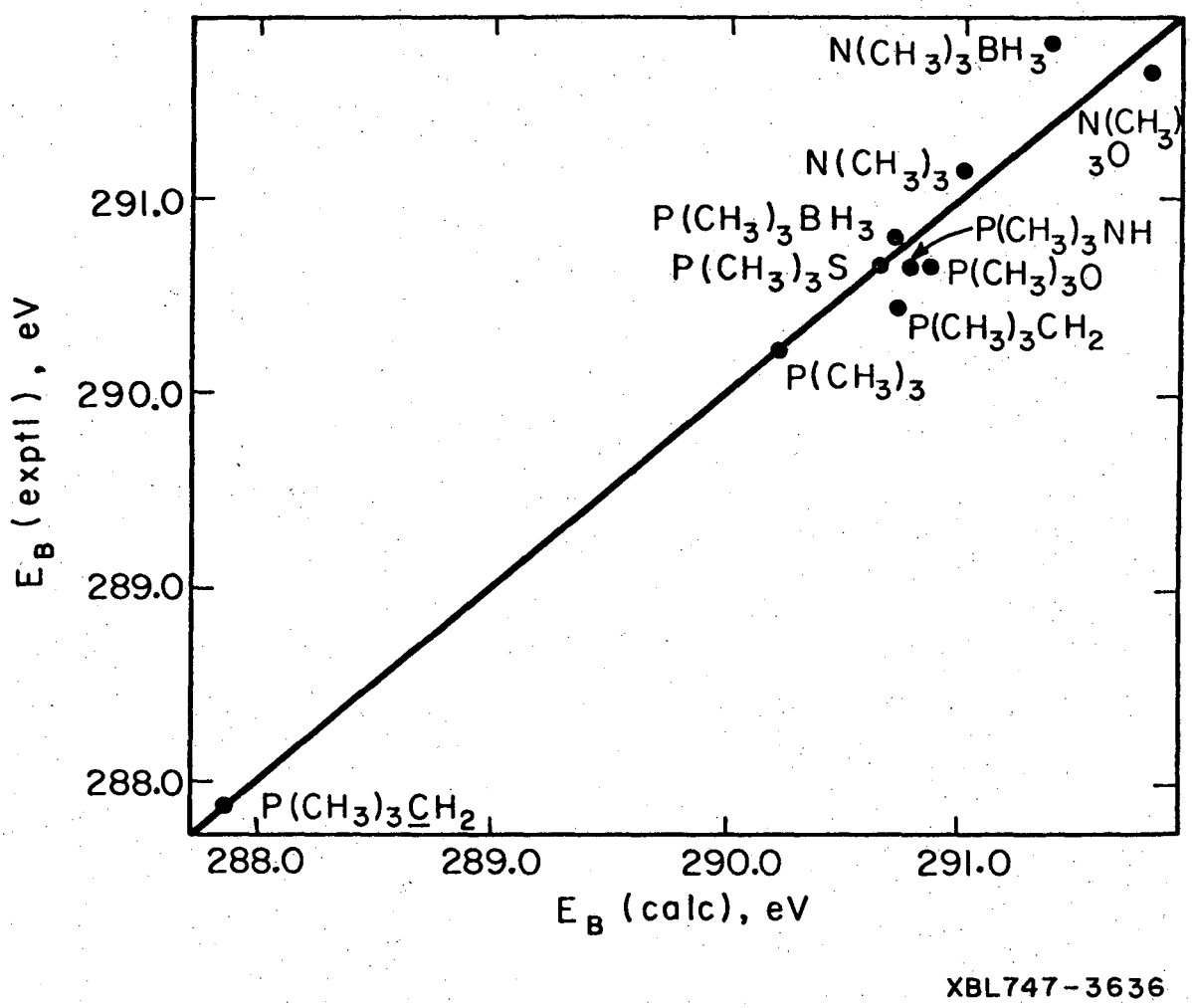

Fig. 1

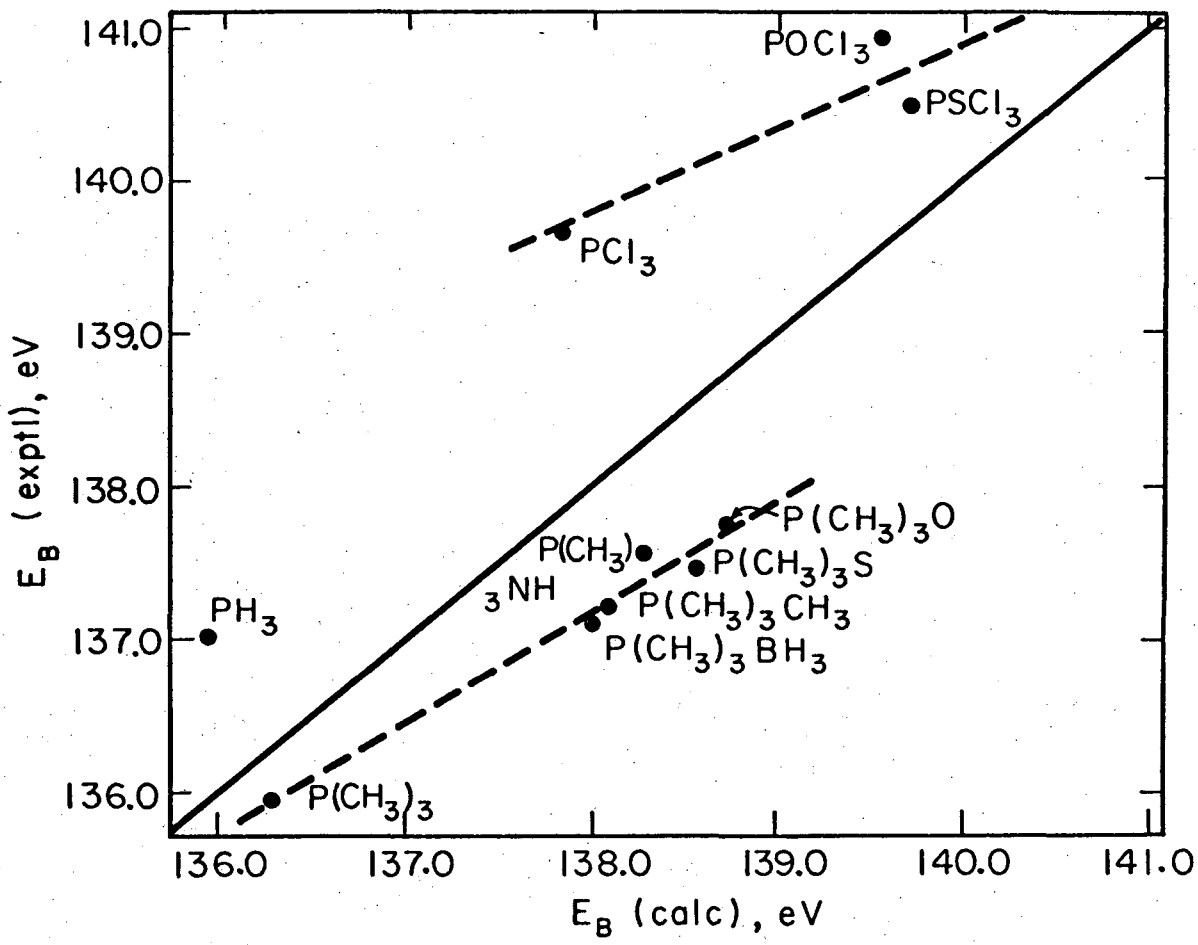

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Fig. 2

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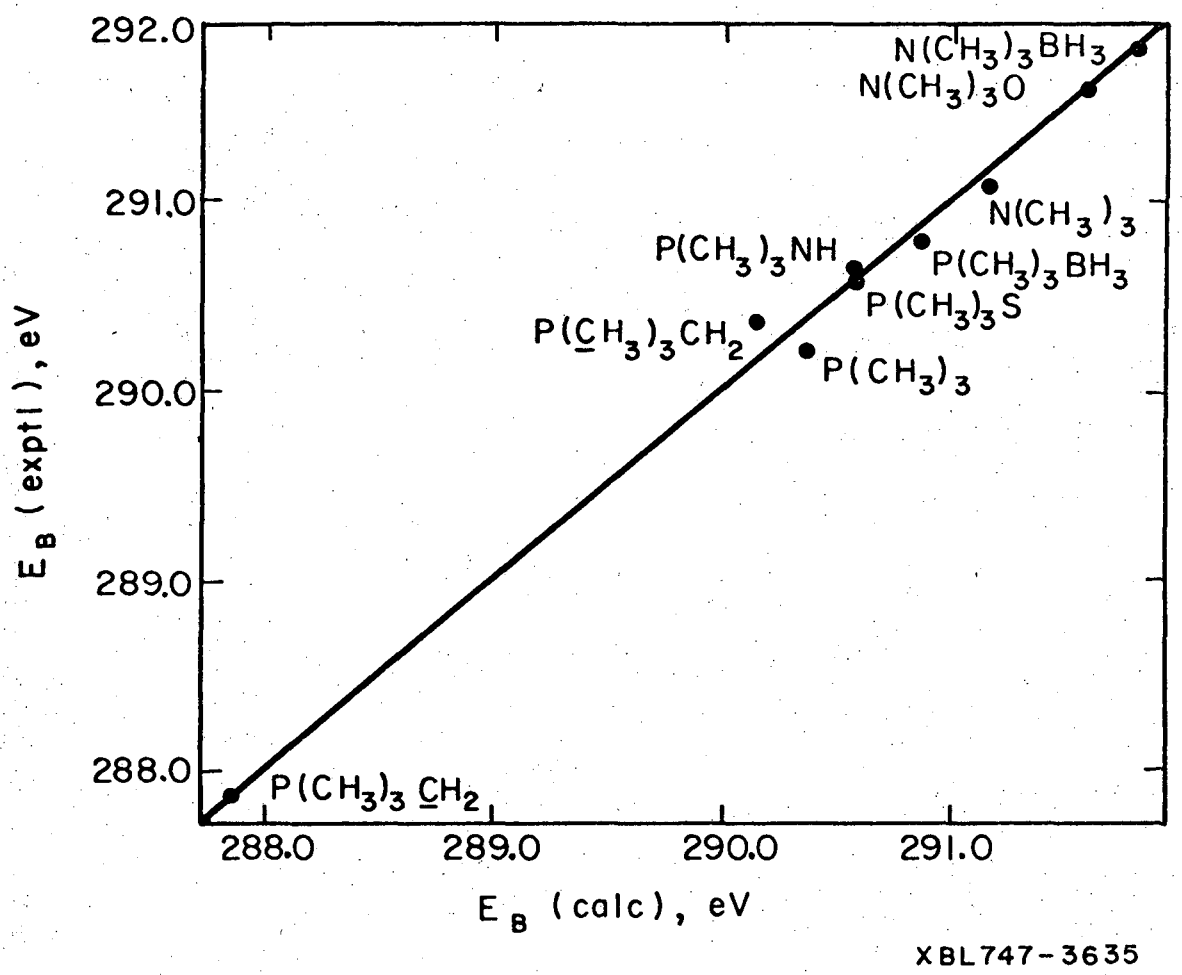
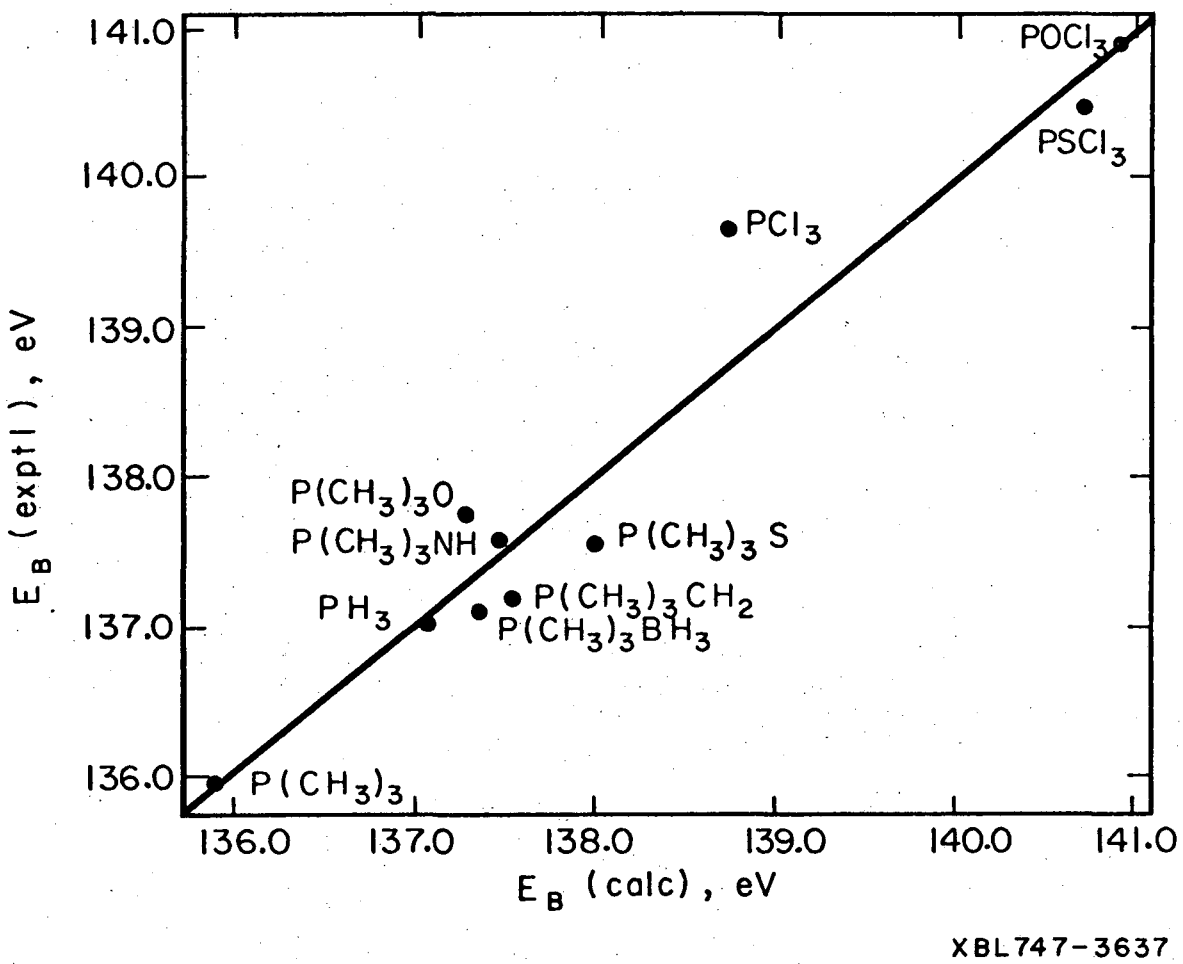


Fig. 3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$P(CH_3)_3S$
PH_3
$P(CH_3)_3CH_2$
$P(CH_3)_3BH_3$
$P(CH_3)_3$
XBL747-3637

Fig. 4

0 0 0 0 4 2 0 0 8 7 3

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