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LAWRENCE RADIATION LABORATORY
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PHOSPHORUS 2$\underline{p}$ ELECTRON BINDING ENERGIES

CORRELATION WITH EXTENDED HUCKEL CHARGES

M. Pelavin,[1] D. N. Hendrickson,[2] J. M. Hollander[1]

and W. L. Jolly[2]

ABSTRACT

Phosphorus 2$\underline{p}$ electron binding energies were measured for 53 phos-

phorus compounds. Phosphorus atom charges, calculated for some of the

compounds by means of a non-iterative as well as an iterative extended

Huckel molecular orbital method, are correlated with the measured phosphorus

2$\underline{p}$ binding energies. The electronic structure of the cyclic phosphonitrilic

chloride trimer, $(NPCl_2)_3$, is briefly discussed.

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I. Introduction

Core-electron binding energies, as determined by x-ray photoelectron spectroscopy, have been found to be chemically shifted and to be correlated to effective atomic charge.[3] Thus core-electron binding energies have been shown to be correlated to formal oxidation states in sulfur[3,4] and chlorine[3,5] compounds and to fractional atomic charges in sulfur,[3] nitrogen[6,7] and carbon[8] compounds. The methods for calculating the fractional atomic charges used in these correlations include a modification of Pauling's method,[9] the CNDO molecular orbital method,[10] and the extended Hückel molecular orbital (EHMO) method.[11]

In this paper, an attempt is made to correlate phosphorus 2$\underline{p}$ electron binding energies with phosphorus atom charges calculated by the EHMO method. The simple EHMO method as well as an iterative variation[12] of the EHMO method are used to calculate the phosphorus atom charges, and the phosphorus atom input parameters are varied to find the set which gives the best correlation of binding energy with calculated charge.

II. Experimental

Photoionization of the phosphorus 2$\underline{p}$ electrons was accomplished by using $Mg_{K\alpha}$ x-radiation (1253.6 eV). A description of the iron-free, double-focusing magnetic spectrometer used to determine the kinetic energies of the photoelectrons has appeared previously[3,13]. In this study, as in previous studies, the carbon 1$\underline{s}$ signal from the pump oil which

formed as a film on the samples served as a convenient reference. For all compounds three measurements of the phosphorus peak were carried out, each followed by calibration with the pump oil carbon peak.

All the phosphorus compounds studied were solids; powdered samples were brushed onto double-faced conducting tape mounted on an aluminum plate, which served as a heat and electron sink. Some instances of decomposition (x-ray induced, thermal, or chemical) were noticed and will be mentioned in the results section.

Some of the phosphorus compounds were purchased; many were kindly provided by Dr. J. Van Wazer. $\underline{Trans}$-$Mn(CO)_4P(C_6H_5)_3Cl$, $\underline{(cis}$-$PP)Mn(CO)_3I$[14], and $Mn(CO)_3(AP)I$[14] were supplied by Dr. G. Nelson, and compounds 46-50 were obtained from L. Kramer. Samples of $(NPCl_2)_3$,[15] $(NaPO_2NH)_3$,[15] P_4OH,[16] and trans-$Rh(CO)Cl(P(C_6H_5)_3)_2$[15] were prepared by standard synthetic procedures.

III. Theory

The theoretical aspects of the determination of core-electron binding energies have been considered previously.[3,7,17] The core-electron binding energy E_b is referred to the Fermi level of the sample. Knowledge of the energy of the x-radiation, E_{x-ray}, the kinetic energy of the photoelectron, E_{kin}, and the work function of the spectrometer material (aluminum), $\phi_{spec.}$, allows the calculation of the core-electron binding energy

$$E_b = E_{x-ray} - E_{kin} - \phi_{spec.}$$

The binding energies of core electrons are influenced by potentials

arising from the net charge on atoms in the particular molecule as well as by the lattice potential of neighboring molecules.[3,7,17] It has been found that the binding energy increases with increasing oxidation state (i.e. actually the effective charge) of the particular atom.

IV. Calculations

Two basic modifications of the extended Hückel molecular orbital method were used. In both cases computations were performed with a CDC 6600 computer using a Fortran IV program. The first modification was that formulated by Hoffmann.[11] In the extended Hückel method no assumptions have to be made concerning hydridization. The Coulomb integrals were approximated by valence state ionization potentials (vsip) as determined by Hinze and Jaffé.[18] The ionization potential for a phosphorus $3\underline{d}$ electron was taken as 3.00 eV.[19] Orbital exponents were secured by using Slater's rules[20] except where noted. Calculations were completed with use of three variations for the off-diagonal Hamiltonian elements: the arithmetic mean $\Big($Equation (1)$\Big)$, the geometric mean $\Big($Equation (2)$\Big)$, and Cusach's approximation[21] $\Big($Equation (3)$\Big)$

$$H_{ij} = 1.75 S_{ij} (H_{ii} + H_{jj})/2 \tag{1}$$

$$H_{ij} = 2 S_{ij} (H_{ii} H_{jj})^{1/2} \tag{2}$$

$$H_{ij} = S_{ij} (H_{ii} + H_{jj}) (2 - |S_{ij}|)/2 \tag{3}$$

Here H_{ii} is the negative of the vsip and S_{ij} is the usual overlap integral.

The second modification of the extended Hückel method used in this work was an iterative type.[12] The Coulomb integrals were set equal to the negative of the appropriate neutral atom vsip's, corrected for net atomic charge q_i where K was taken as 2.00 eV per unit charge.

$$H_{ii} = H_{ii}^{\circ} - Kq_i \qquad (4)$$

The Slater exponents μ_i were also taken as charge dependent, assigned by an extension of Slater's rules.

$$\mu_i = \mu_i^{\circ} + 0.35q_i/n^*$$

Here n^* is the effective principal quantum number and μ_i° is the exponent for the ith orbital on a neutral atom. The net atomic charges q_i were obtained in each cycle by an application of Mulliken's population analysis.[22] In our self-consistent extended Hückel calculations we elected to use the Cusach approximation $\left(\text{Equation (3)}\right)$ for the off-diagonal Hamiltonian elements. The calculational procedure consisted of iterating until the atomic charges were self-consistent to at least 0.01.

Cartesian coordinates were obtained from Program PROXYZ;[23] the molecular parameters were obtained from crystal structure determinations[24-26] or from estimates.

Phosphorus atomic charges were also calculated by the simple Pauling method.[9] The ionic character (I_{AB}) of a bond between atoms A and B is taken as a function of the atom electronegativities χ_A and χ_B.

$$I_{AB} = 1.0 - e^{-0.25(\chi_a - \chi_B)^2} \tag{4}$$

The atom electronegativities can be taken as charge-dependent functions, the prescription for correction of neutral atom electronegativities being simply that the electronegativity is increased $\frac{2}{3}$ of the way to the electronegativity of the element next in the periodic table for each unit positive charge. Hydrogen cannot be treated by this simple correction formula, but it was found that the phosphorus charges in the molecules studied in this work were affected only slightly by correcting χ_H for charge by some reasonable amount.

Within the valence-bond formalism the net charge q_A on an atom A is given by

$$q_A = Q_A + \sum_{B \neq A} I_{AB} \tag{5}$$

where Q_A is the formal charge on atom A and the summation is over all the bonds to atom A. The calculational process is iterative because of the charge-dependent atom electronegativities; "self-consistent" atomic charges result. In no case did we use a valence bond representation indicative of 3d phosphorus orbital participation as has been done in the case of sulfur compounds.[3]

V. Result and Discussion

The work function of the spectrometer material was arbitrarily assigned a value of 4.0 eV, for normalization purposes.[7]

Correlation with Charges Obtained from Extended Hückel Molecular Orbitals. Phosphorus 2p electron binding energies determined for over fifty compounds are listed in Tables I and II. The range of binding energy shifts was found to be about 8 eV. In the case of twenty-five of these compounds, non-iterative extended Hückel molecular orbital calculations were made by using Equation (1), both without and with 3d orbitals on the phosphorus atom. The resultant phosphorus atom charges are given in Table I. It can be seen that the calculated phosphorus atom charge is, except in a few cases, unaffected by inclusion of 3d orbitals.

In Figure 1 the measured phosphorus 2p binding energies are plotted against the non-iterative extended Hückel-calculated phosphorus charges. The correlation of these two quantities can be seen to be poor. This is in contrast to our nitrogen work[7] where a reasonably good correlation was found with the same variation of the non-iterative extended Hückel method (i.e. the arithmetic mean off-diagonal approximation). Extensive modifications of the input data were tried (see Table III). The phosphorus 3d orbital was contracted by arbitrarily assigning the Slater exponent a value of 1.6 (this value is in the range suggested by Fogleman et al[27]) The effect of this can be seen to be negligible for the series of molecules in Table III.

In the second modification the phosphorus 3$\underline{d}$ orbital was contracted and its vsip was changed from 3.0 eV to 7.0 eV (see Column 3, Table III). The resultant phosphorus charges were appreciably changed, but the correlation was not markedly improved for the seven compounds considered. The last two columns in Table III list the phosphorus charges resulting from changing the input vsip's for the phosphorus 3$\underline{s}$ and 3$\underline{p}$ orbitals. Again, a plot of the data shows little improvement in the correlation. Finally, the character of the off-diagonal approximation used in our non-iterative extended Hückel calculations was changed to both the geometric mean $\Big($Equation (2)$\Big)$ and the Cusach variation $\Big($Equation (3)$\Big)$. The calculated phosphorus atom charges in a series of nine compounds for both of these approaches is given in Table IV. The data obtained using the Cusach and geometric mean approximations showed essentially the same correlation as found in Figure 1.

It seemed at this point that the inability to obtain even a moderate correlation of measured phosphorus 2$\underline{p}$ binding energy with non-iterative extended Hückel-calculated phosphorus charge was a manifestation of some inherent problem(s) in the calculational method. This belief was nurtured, as stated above, by our success with nitrogen 1$\underline{s}$ data[7] as well as with recent boron 1$\underline{s}$ data.[28] Concerning the reality of phosphorus atom charges obtained from this simple extended Hückel method, Sichel and Whitehead[29] have found a good linear correlation of the phosphorus nuclear magnetic resonance chemical shifts of the methylphosphines with calculated charges on phosphorus. Unfortunately this is not a diversified series of phosphorus compounds. An attempt to correlate the phosphorus charges given in Table I with reported phosphorus chemical shifts[30] was a marked failure.

This failure could be attributed either to some inadequacy in the non-iterative extended Hückel method (applied to phosphorus compounds) or more probably to differing average electronic excitation energies[31] throughout the series of molecules.

Considering the distribution of points in Figure 1, it is interesting to note that compounds 10-24 are molecules containing P-O bonds. Perhaps the simple extended Hückel method has tended to overemphasize the polarity of these P-O bonds and as such has assigned excessive positive charge to the phosphorus atoms. It does seem unrealistic that the phosphates 13, 22, and 24 should have essentially the same net phosphorus charges as that obtained for the hexafluorophosphate ion (1). Some support for this proposal of overemphasis of P-O bond polarity can be gained by reverting to two variations of the Pauling method[9] of calculation of net atomic charges.

In analogy with our non-iterative extended Hückel calculations, phosphorus charges for the compounds in Figure 1 were obtained by a straightforward application of Equations (4) and (5), using neutral-atom electronegativities. The resultant charges are plotted in Figure 2 vs. the phosphorus 2p binding energies. The similarity of distribution of points in Figures 1 and 2 is striking. If the other modification of the Pauling method is invoked we would expect this iterative "self-consistent" method to accomplish two goals: 1) overall decrease in all net charges, and 2) reduction in tendency to overemphasize particular bond polarities. In Figure 3 we can clearly see that the first expectation is met; the

the phosphorus charge range is essentially halved from that in Figure 2. The improved correlation depicted in Figure 3 tends to support the second expectation.

Having accepted this interpretation of the lack of correlative ability, it seemed reasonable that a more modern version of the extended Hückel method would be warranted, a version where the Hamiltonian is charge dependent.[12] Using charge-dependent valence state ionization potentials $\left(\text{Equation (4)}\right)$ coupled with the Cusach approximation $\left(\text{Equation (3)}\right)$ for the off-diagonal Hamiltonian terms, we obtained the phosphorus charges given in Table I. All phosphorus charges are appreciably reduced when using this iterative extended Hückel method. In fact the same order of reduction occured in this case as with the simple Pauling method. Unfortunately, these self-consistent extended Hückel-calculated phosphorus charges gave little improvement in the correlation with phosphorus 2$\underline{p}$ binding energies (see Figure 4).

Although at this point one might tend to lose hope of obtaining a good correlation, it must be remembered that the iterative extended Hückel method used here still contains a gross approximation. The charge correction of all vsip's by the same factor seems unrealistic. A better approach would be to use valence orbital ionization potentials, which have been tabulated for the atoms as a function of charge and configuration.[32]

Electronic Structure of Phosphonitrilic Chloride Trimer. As a by-product of this study we obtained an extended Hückel description of the cyclic phosphonitrilic chloride trimer $\left((NPCl_2)_3\right)$. Calculations were completed with use of a planar structure for $(NPCl_2)_3$ coupled with known

molecular dimensions.[24] Two different descriptions have been given for

the electronic pi system above and below the plane of the ring.

Dewar et al[33] concluded that there are "islands" of π character, each

involving three-centered π-bonds centered at a nitrogen atom. Craig

and Paddock[34] suggested unequal participation of the $3d_{xz}$ and $3d_{yz}$

(the molecular plane is the x-y plane) orbitals would result in a

continuous pi molecular orbital around the ring.

The π type (e'' and a_2'' in D_{3h}) molecular orbitals resulting from

both the non-iterative and iterative extended Hückel treatments showed

unequal $3d_{xz}$ and $3d_{yz}$ participation, in agreement with the suggestion of

Craig and Paddock. The $3d$ participation was somewhat greater in the

iterative case. In both cases the molecular orbital ordering was found

to be $\cdots\cdots e'(2)e''(2)a_2''(2)a_2''^*a_1'^*\cdots\cdots$. The ionization potential of

$(NPCl_2)_3$ has been determined to be 10.26 eV,[35] which compares with the

eigenvalve of the highest filled orbital, a_2'' (-12.00 eV in the iterative

calculation). The electronic spectrum of $(NPCl)_3$ has a broad peak at

199mμ(6.23 eV).[36] The iterative calculations predict an $^1E'$ ($a_2''^* \leftarrow e''$)

transition at 8.77 eV consisting essentially of the transition of a

nitrogen $2p_z$ electron into the phosphorus $3d$ orbitals.

Decompositions. In the case of some of the compounds studied two

peaks were observed in the P_{2p} spectrum where only a single peak was

expected. It was usually easy to assign the peak arising from the compound

under study, either by peak position or by observing a change in the

relative areas of the two peaks. Both elemental red phosphorus and

tetraphosphorus trisulfide (see Table I) gave a second peak at 134.5 eV

in addition to their assigned peaks. In each case the assignment was made

on the basis of peak position, since little time dependence was noted
in the spectrum. For red phosphorus the decomposition peak was the
larger, whereas the opposite was found for P_4S_3. This probably parallels
their reactivities with water vapor; red phosphorus reacts slowly with
water vapor and oxygen at normal temperatures, while under "ordinary
conditions" P_4S_3 is unaffected by exposure to the atmosphere.[37] In
fact the red phosphorus oxidation is accelerated markedly by small
concentrations of silver (we used silver-based conducting tape!).[38]
The decomposition product in each of these cases is then a mixture of the
oxyacids of phosphorus, which probably had formed on the surface before
we loaded the samples into the spectrometer.

The appearance of two peaks (see Table II) in the spectra of the
metal phosphides CrP and MnP is not easily explained. Hydrolysis of
a phosphide should give only gaseous phosphine, but apparently there was
some surface oxidation.

Two phosphorus peaks would be expected for the compound P_4OH probably
in the ratio of 3:1.[39] As noted in Table II a sample of P_4OH (1 day old)
gave two peaks in the ratio of 2:1 with binding energy values of 129.9
and 133.1 eV, respectively. A portion of the same sample was stored for
a week in a capped bottle and the phosphorus spectrum rerun. Two peaks
were again found, still in the ratio of 2:1. The smaller peak, however,
had moved to a binding energy of 134.0 eV while the larger peak remained
fixed. The sample was then kept in air overnight and the phosphorus
spectrum rerun. This spectrum showed peaks at 130.0 and 134.0 eV
binding energy in the ratio of 1:1. Apparently we were observing
initially the P_4OH 3:1 pattern with some surface (or bulk?) impurity.

Applications. The effect of metal coordination on the charge of a ligand atom can be studied by this method. From the measurements on triphenylphosphine, the triphenylphosphine coordinated complexes (Table II, compounds 26 and 29), and the phosphonium salt, compound 53, it can be seen that coordination of the triphenylphosphine ligand decreases the charge on the phosphorus atom. This is analogous to results obtained for the NH_3 ligand.[7]

Unfortunately it does not seem that at present phosphorus photoelectron spectroscopy on biological compounds will be definitive, at least insofar as the type of phosphorus atom is concerned. This can be seen by the small changes in binding energy for the compounds 46-50 in Table II.

Table I.

Phosphorus 2$\underline{p}$ Binding Energies and
Extended-Hückel Calculated Charges

Compound Number	Compound	Binding Energy eV.	Calculated Phosphorus Atom Charge		
			Non-Iterative[d]		Iterative[e]
			Without 3$\underline{d}$	With 3$\underline{d}$	With 3$\underline{d}$
1	NH_4PF_6	137.3	3.723	3.806	2.505
2	$(NPCl_2)_3$	134.5	2.321	2.277	0.961
3	$(CH_3PS_2)_2$	133.4	1.502	1.591	0.764
4	P_4S_{10}	134.0	1.515	1.390	
5	$(C_6H_5)_3PS$	132.3		2.194	
6	$n\text{-}(C_4H_9)_4P^+Cl^-$	132.3	1.173	2.525	
7	$(C_6H_5)_3P$	130.6		0.999	
8	P_4S_3	130.5[b]	0.324[c]	0.338[c]	0.303[c]
			0.048	0.148	0.122
9	P_{red}	130.1[b]	0	0	0
10	KPF_2O_2	134.8	3.578	3.547	1.956
11	$(NH_4)_2PFO_3$	134.1	3.490	3.443	1.815
12	$Na_2H_2P_2O_7$	133.9	3.387	3.387	1.767
13	KH_2PO_4	133.9		3.669	1.785
14	$(NH_4)_2CH_3PO_3$	133.8	2.905	3.041	1.435
15	$C_6H_5CH_2PO_3H_2$	133.8	2.846	3.284	
16	$HOPO(NH_2)_2$	133.6	2.832	3.083	1.465
17	$Na_4P_2O_7$	133.3	3.374	3.354	
18	Na_3PSO_3	133.0	2.936	2.622	1.361
19	$Na_3(PO_2NH)_3$	133.0	2.892[a]	3.062[a]	

Compound Number	Compound	Binding Energy eV.	Calculated Phosphorus Atom Charge		
			Non-Iterative[d]		Iterative[e]
			Without $3\underline{d}$	With $3\underline{d}$	With $3\underline{d}$
20	$BaHPO_3$	132.9	2.844	2.790	1.420
21	$(C_6H_5)_3PO$	132.7		2.744	
22	K_2HPO_4	132.7		3.621	2.001
23	$KH_2PO_2 \cdot H_2O$	132.4	2.236	2.201	1.189
24	Na_3PO_4	132.1	3.413	3.621	1.544
25	P_4S_7	134.3		1.370	
		132.7		0.266	

[a] Calculation with assumed $r_{P-N} = 1.70\text{Å}$.

[b] A second peak at 134.5 eV. was attributed to a decomposition product.

[c] There are two different types of phosphorus in P_4S_3; the more positive number in each case refers to the unique phosphorus atom. For purposes of plotting an average charge value was used.

[d] Completed using arithmetic off-diagonal approximation $\left(\text{Equation (1)}\right)$.

[e] Charges are self-consistent to at least 0.01.

Table II.

Some Phosphorus 2p Binding Energies

Compound Number	Compound	Phosphorus 2p Electron Binding Energy eV.
26	$Mn(CO)_4P(C_6H_5)_3Cl$	131.2
27	$(cis-PP)Mn(CO)_3I$[a]	133.2
28	$Mn(CO)_3(AP)I$[b]	133.0
29	$trans-Rh(CO)Cl(P(C_6H_5)_3)_2$	131.6
30	Trisα-napthylphosphine	130.9
31	$ortho-[(C_6H_5)C_6H_5]_3P$	134.3
32	P_3N_5	133.2
33	$(NaPO_3)_3$	134.0
34	$(NaPO_3)_4 \cdot 4H_2O$	134.1
35	P_4OH	129.9[c]
		133.1
36	Phosphotungstic acid	133.0[d]
37	$(C_6H_5O)_3PO$	134.2
38	$(C_6H_5S)_3P$	134.4
39	$Na_5P_3O_{10}$ Form I	133.6
40	$NaPO_3$ glass	134.5
41	P_4S_5	132.0
		134.9(shoulder)
42	BP	129.5
43	$cis-PP$[a]	131.3
		132.6(shoulder)

Compound Number	Compound	Phosphorus 2p Electron Binding Energy eV.
44	PBr_5	138.4^e
45	$POBr_3$	134.4
46	Riboflavin-5´-phosphate	133.5
47	O-phosphoserine (dl)	133.5
48	Barium phosphoglyceric acid	133.5
49	O-phosphothreonine (dl)	133.7
50	O-phosphoethanolamine	134.1
51	CrP	128.8^f
52	MnP	129.3^g
53	$(C_6H_3CH_2)(C_6H_5)_3P^+Cl^-$	132.5

[a] The ligand cis-PP is the bidentate 2-cis-propenylphenyl-diphenylphosphine.

[b] The ligand AP is the bidentate 2-allylphenyldiphenylphosphine.

[c] Two peaks observed for P_4OH in the ratio of about 2:1, the lower binding energy peak the larger. See the discussion for further particulars.

[d] A second peak at 134.2 eV. was observed, attributed to something other than starting material, for peak increased between successive scans while the 133.0 eV. peak decreased.

[e] A second larger peak was found at 134.4 eV., probably assignable to the oxidation product $POBr_3$.

[f] A second peak was observed at 133.8 eV., due probably to an oxidation product.

[g] A second peak was observed at 133.2 eV., due probably to an oxidation product.

Table III.

Non-Iterative Extended Hückel-Calculated[a]
Net Phosphorus Atom Charges Resultant From
Various Input Parameter Modifications

	Phosphorus Atom Charge and Input Parameter Modification			
Molecule	$\mu(P_{3\underline{d}})=1.6$	$\mu(P_{3\underline{d}})=1.6$ $vsip(P_{3\underline{d}}^-)=7.0eV.$	$vsip(P_{3\underline{s}}^-)=17.0$	$vsip(P_{3s})=16.0$ $vsip(P_{3\underline{p}}^-)=11.5$
$PFO_3^=$	3.442	2.880	3.579	3.761
$PSO_3^=$	2.746	1.943	2.881	3.096
$PF_2O_2^-$	3.554	3.057	3.683	3.858
$(CH_3PS_2)_2$	1.215	0.494	1.709	2.022
P_4S_3	0.260[b]	-0.181[b]	0.437[b]	0.690[b]
	0.019	-0.202	0.196	0.305
PF_6^-	3.792	3.259	3.933	4.086
$HPO_4^=$	3.524	3.054	3.810	4.017

[a] Equation (1) used for off-diagonal terms.

[b] See footnote c in Table I.

Table IV.

Non-Iterative Extended Hückel-Calculated
Net Phosphorus Atom Charges Resultant From
Two Off-Diagonal Approximations

Molecule	Phosphorus Atom Charge	
	Geometric H_{ij} [a]	Cusach's H_{ij} [b]
$PF_2O_2^-$	4.191	3.739
$PFO_3^=$	4.131	3.676
$PSO_3^{\equiv}$	3.610	3.205
$(CH_3PS_2)_2$	2.963	2.182
P_4S_3	0.993[c]	0.870
	0.464	0.276
PF_6^-	4.574	4.198
$HPO_4^=$	4.402	4.068
$PO_4^{\equiv}$	3.727	3.305

[a] Equation (2).

[b] Equation (3).

[c] See footnote c in Table I.

FIGURE CAPTIONS

Figure 1. Plot of phosphorus 2p binding energies vs. non-iterative extended Hückel-calculated charges on phosphorus atoms.

Figure 2. Plot of phosphorus 2p binding energies vs. phosphorus atom charges calculated by Pauling method using neutral atom electronegativities.

Figure 3, Plot of phosphorus 2p binding energies vs. phosphorus atom charges calculated by Pauling method using charge-dependent atom electronegativities.

Figure 4. Plot of phosphorus 2p binding energies vs. iterative extended Hückel-calculated charges on phosphorus atoms.
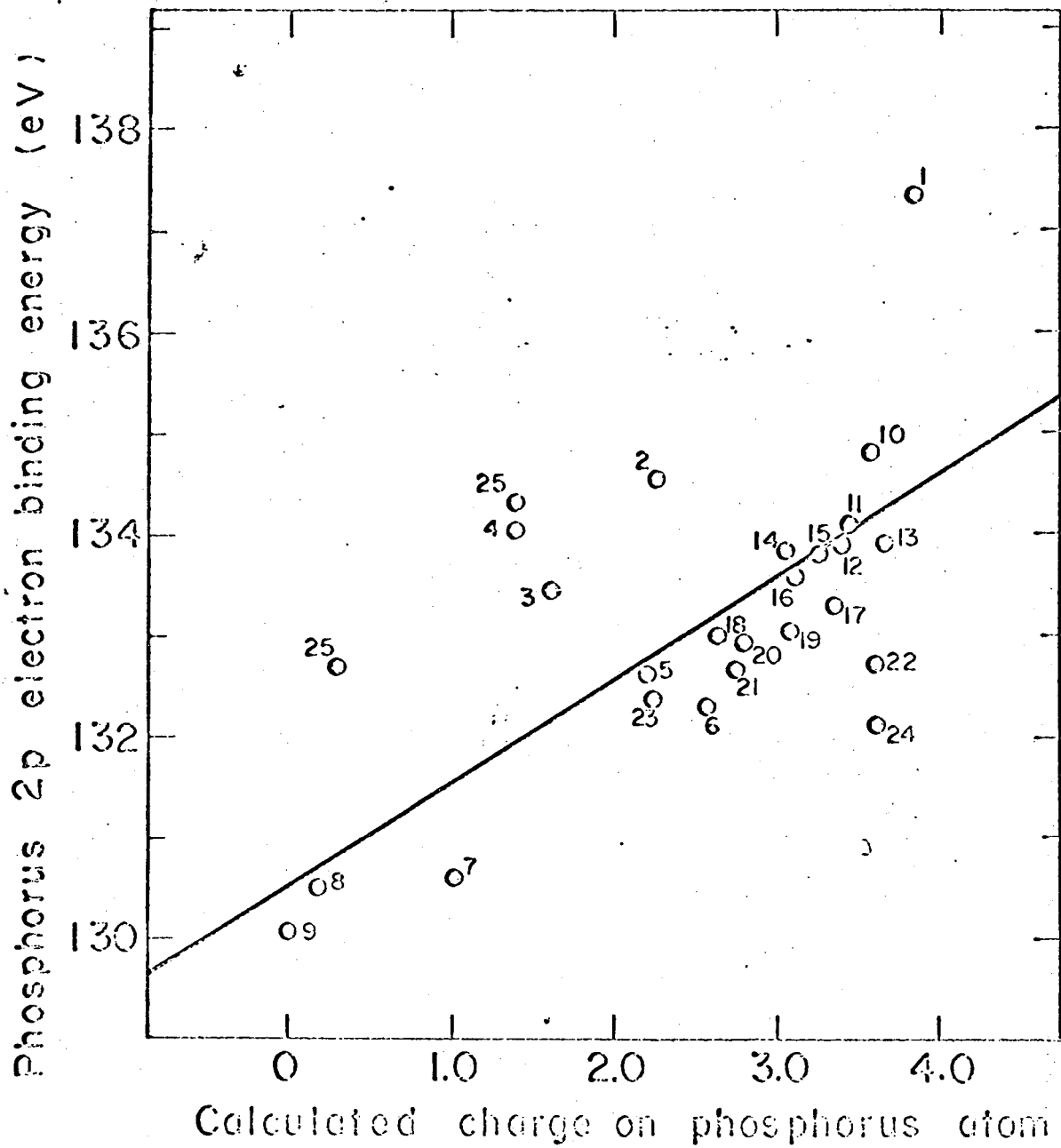
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Fig. 1
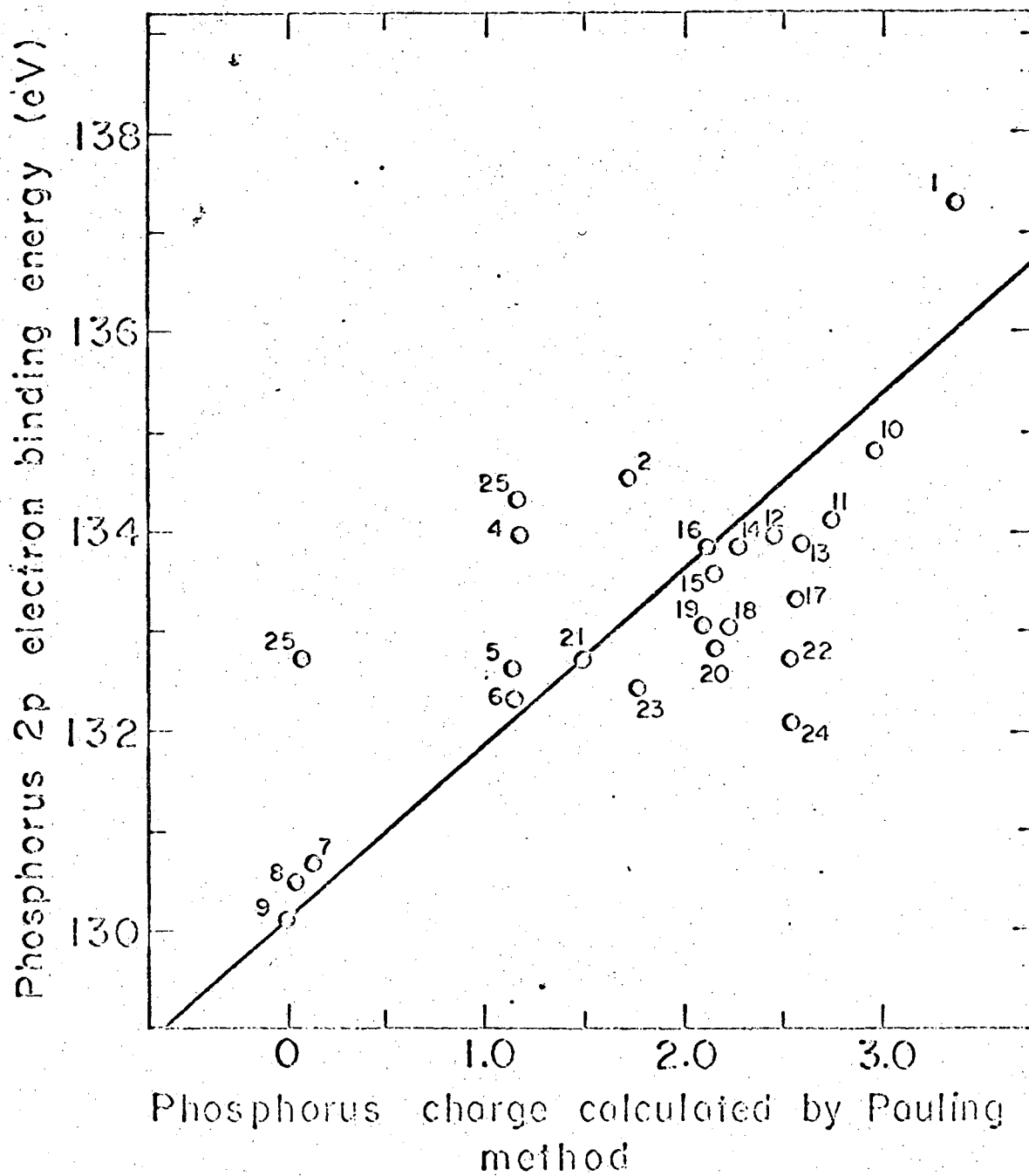
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Fig. 2
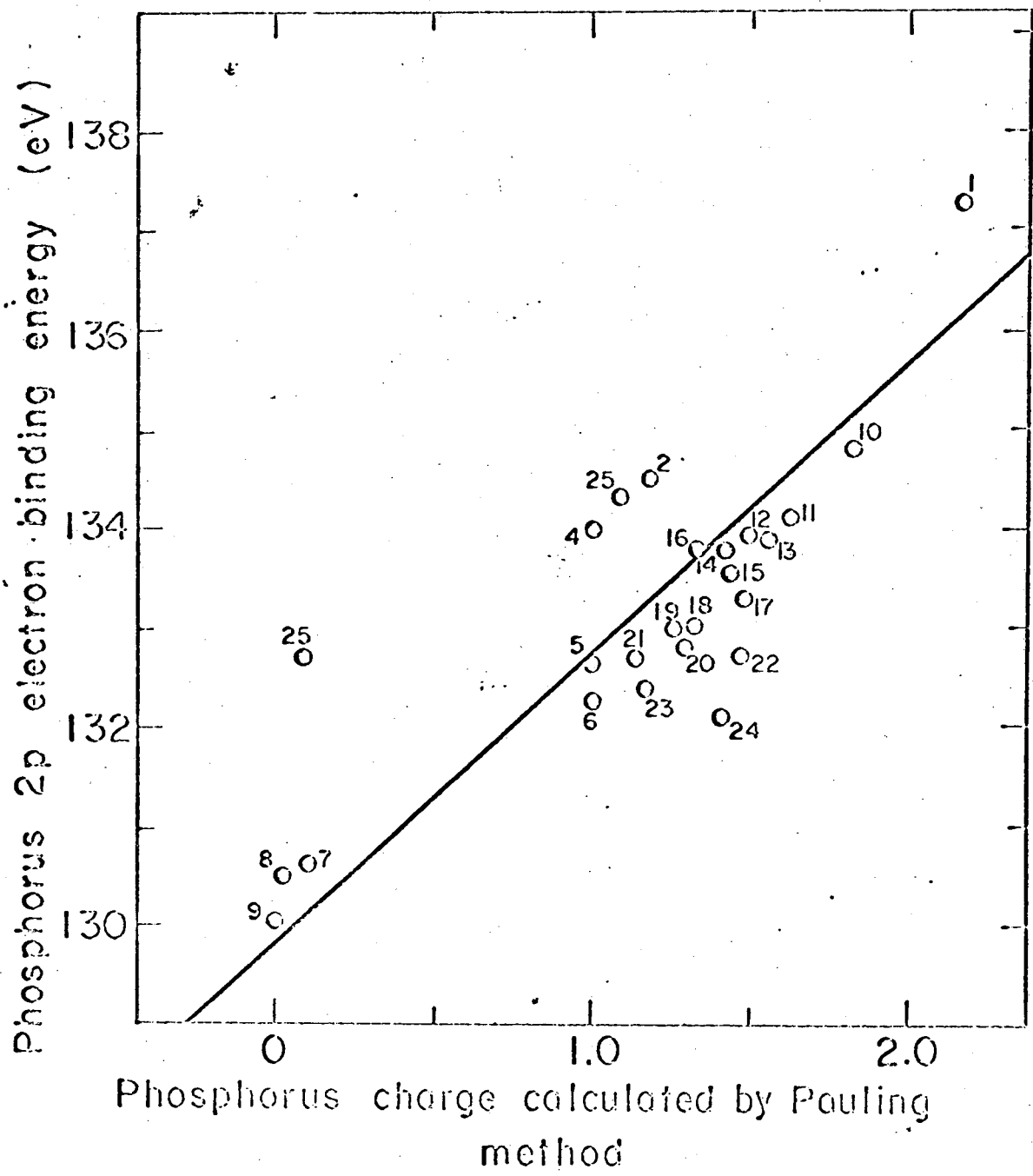
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Fig. 3
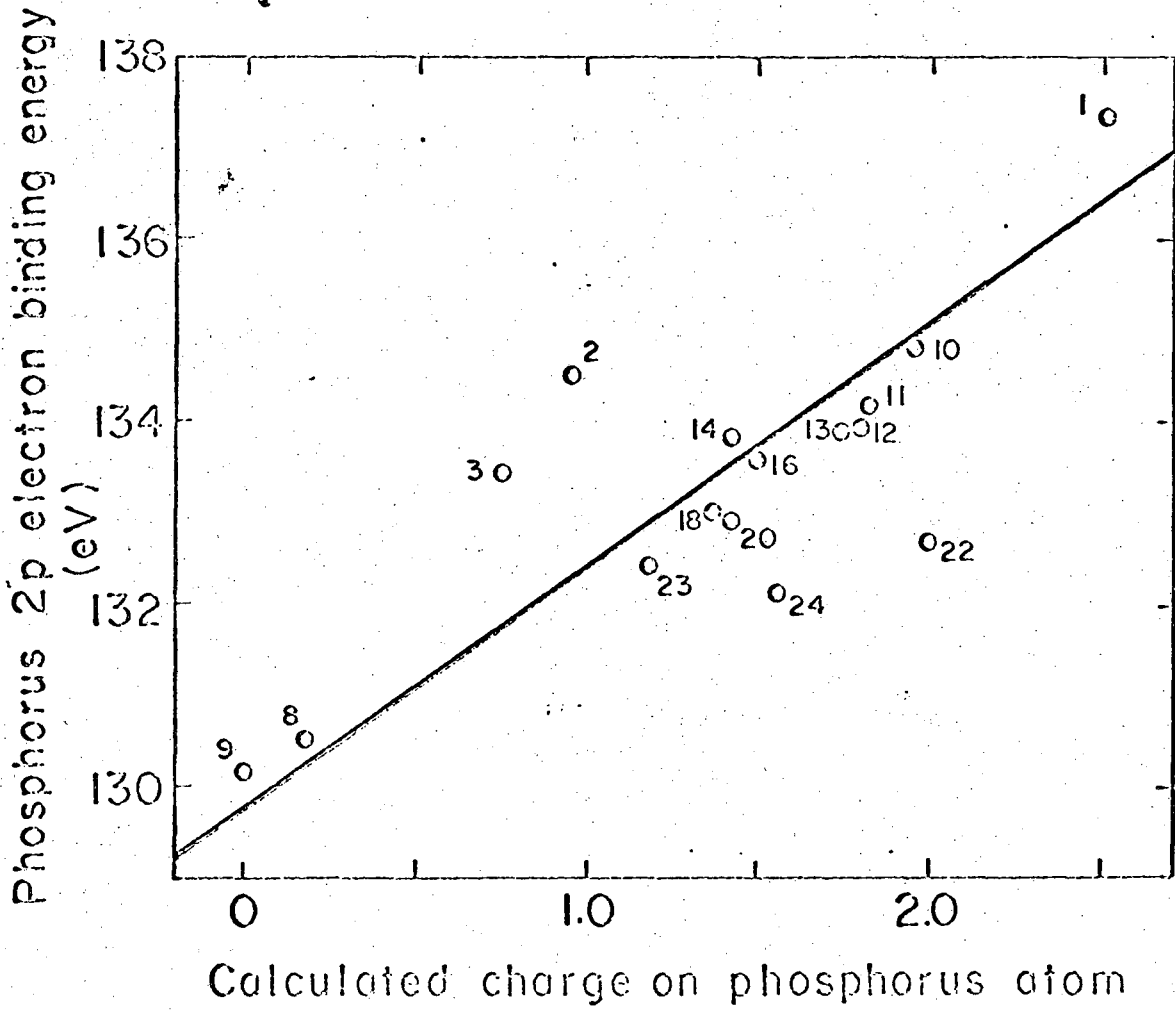
XBL696-2990

Fig. 4

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