of Cd–O bonding distances. Prompted by an anomaly between the observed shielding anisotropies of the magnetically inequivalent ^{113}Cd in $3CdSO_4{\cdot}8H_2O$ and the proposed Cd–O bonding distances, a refinement[10] of the X-ray crystal structure of this salt has shown a much more uniform distribution of Cd–O bonding distances than was originally[3] proposed.

Acknowledgment. The authors thank (1) Dr. H. F. Franzen and Robert Kematick for the Guinier X-ray powder measurements and other discussions; (2) Gary Austin and Robert Hofer of the Ames Lab Analytical Services for the determinations of H_2O/Cd mole ratios, and (3) Gary Robbins for assistance in the use of ORTEP to draw the various crystal structures.

UPE Studies of Conjugation Involving Group 5A Elements. 1. Phenylphosphines

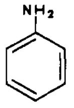
Diane E. Cabelli, Alan H. Cowley,* and Michael J. S. Dewar*

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received October 15, 1979

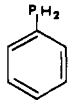
Abstract: UPE spectra are reported for phenylphosphine, *p*-phenylenediphosphine, phenyldichlorophosphine, *p*-phenylenebis(dichlorophosphine), phenylbis(diethylamino)phosphine, and *p*-phenylenebis(diethylamino)diphosphine. Analysis using PMO theory indicates that the assignments in phenylphosphine and aniline are similar, I_1 in each case corresponding to ionization from a perturbed benzene π MO, I_3 to a perturbed lone pair. This conclusion agrees with the well-established assignment for aniline but differs from that previously suggested for phenylphosphine. Our conclusions are supported by MNDO calculations.

A problem which has remained of topical interest for many years concerns the extent to which trivalent elements of group 5A can undergo conjugative interactions with the π electrons of adjacent conjugated systems via their lone pair electrons. The existence of such interactions has long been recognized in the case of nitrogen, as, for example, between nitrogen and the benzene ring in aniline (**1**). Here the interaction leads to changes in chemical behavior, as exemplified by the low basicity of **1**. Effects of this kind are, however, likely to be smaller in the case of other group 5A elements, in particular phosphorus.

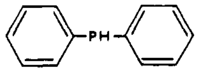
The development of ultraviolet photoelectron (UPE) spectroscopy has provided a valuable tool for studying conjugative interactions in molecules,[1] on the basis of interpretation of UPE spectra in terms of MO theory and Koopmans' theorem.[2] Studies of this kind have established the existence of strong conjugative interactions in unsaturated amines such as **1**[3] and also in phenylphosphine (**2**).[4] Some confusion seems to have been caused here by failure to distinguish between collective and one-electron properties of molecules.[5] It is quite possible for conjugative interactions to lead to large changes in the energies of individual MOs (and hence in one-electron properties associated with those MOs) without significantly affecting the total energy of the molecule (and hence its collective properties). The UPE data for **1** and **2** therefore give no indication of the extent to which the observed conjugative interactions will affect their chemical reactivity and other collective properties. Nevertheless the orbital interactions are clearly of interest in their own right.



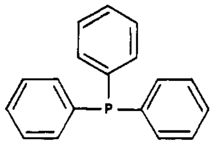
1



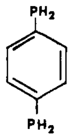
2



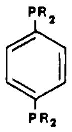
3



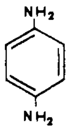
4



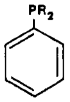
5



6 **a**, R = NEt$_2$
b, R = Cl



7



8 **a**, R = NEt$_2$
b, R = Cl

9

10

$P[NMe_2]_3$

11

Analysis of the UPE spectrum of **2**, using the PMO[6] approach first applied to benzene derivatives by Turner et al.,[7] indicates the existence of a strong conjugative interaction between phosphorus and the ring. The HOMO of benzene consists of a pair of degenerate π MOs which, in real form and C_{2v} symmetry, are indicated in Figure 1. We will follow the usual convention of continuing to use the C_{2v} description (a_2,b_1), even in cases when substitution destroys the C_{2v} symmetry. In **2**, with phosphorus attached to C_1 of benzene (Figure 1), the phosphorus lone pair AO(p) does not interact with the a_2 MO. The ionization corresponding to this should remain virtually unchanged in the UPE spectrum of **2**. Indeed, I_2 for **2** (9.37 eV) is similar to that for benzene (9.24 eV). The small difference can be attributed to miscellaneous second-order effects (inductive effect, field effect, interactions with phosphorus 3d AOs and/or the PH bonds, which, in **2**, do not lie in the nodal plane of the ring). I_1 and I_3 then correspond to the p and b_1 orbitals. The fact that b_1 is considerably

---

(1) See: (a) Turner, D. W.; Baker, A. D.; Baker, C.; Brundle, C. R. "*Molecular Photoelectron Spectroscopy*"; Wiley: New York, 1970. (b) Bock, H.; Ramsey, B. G. *Angew Chem., Int. Ed. Engl.* **1973**, *12*, 734. (c) Rabalais, J. W. "*Principles of Ultraviolet Photoelectron Spectroscopy*"; Wiley: New York, 1977.

(2) Broglie, F.; Clark, P. A.; Heilbronner, E.; Neuenschwander, M. *Angew Chem., Int. Ed. Engl.* **1973**, *12*, 422.

(3) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1977**, *69*, 521.

(4) Debies, T. P.; Rabalais, D. W. *Inorg. Chem.* **1974**, *13*, 308.

(5) See: Dewar, M. J. S. *Chem. Eng. News* **1965**, *43*, 86. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(6) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341, 3345, 3350, 3353, 3355, 3357. Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975.

(7) Turner, D. W.; May, D. P. *J. Chem. Phys.* **1966**, *45*, 471; **1967**, *46*, 1156.

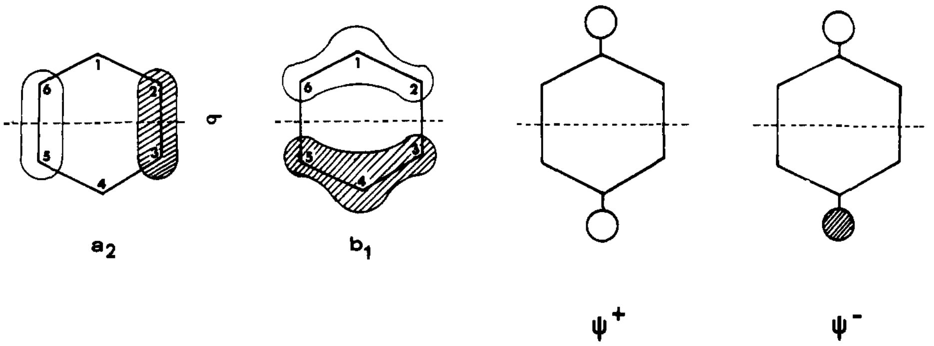


Figure 1. The degenerate HOMOs of benzene, represented in real form with C_{2v} symmetry, and symmetry combinations (ψ^+,ψ^-) of AOs of X in p-$C_6H_4X_2$.

Table I. Lone Pair Ionization Energies of Simple Amines and Phosphines

amine	IE	phosphine	IE
NH_3	10.85[a]	PH_3	10.60[b]
CH_3NH_2	9.7[c]	CH_3PH_2	9.6[d]
$(CH_3)_2NH$	8.9[e]	$(CH_3)_2PH$	9.13[e]
$(CH_3)_3N$	8.54[f]	$(CH_3)_3P$	8.60[f]
NCl_3	10.6[g]	PCl_3	10.52[g]

[a] Potts, A. W.; Lempka, H. J.; Streets, D. G.; Price, W. C. *Philos. Trans. R. Soc. London, Ser. A* 1970, *No. 268,* 59. [b] Branton, G. R.; Frost, D. C.; McDowell, C. A.; Stenhouse, I. A. *Chem. Phys. Lett.* 1970, *5,* 1. [c] Crawford, A. B.; Frost, D. C.; Herring, F. G.; McDowell, C. A. *Can. J. Chem.* 1971, *49,* 1135. [d] Cradock, S.; Ebsworth, E. A. V.; Savage, W. J.; Whiteford, R. A. *J. Chem. Soc., Faraday Trans. 2* 1972, *68,* 934. [e] Unpublished work by Dr. D. W. Goodman. [f] Elbel, S.; Bergman, H.; Ensslin, W. *J. Chem. Soc., Faraday Trans 2* 1974, *70,* 555. [g] Potts, A. W.; Lempka, H. J.; Streets, D. G.; Price, W. C. *Philos. Trans. R. Soc. London, Ser. A* 1970, *No. 268,* 59.

displaced from its position in benzene indicates a rather strong interaction between it and p.

This argument implies that there is a strong interaction between phosphorus and the ring in **2**. The question still remains, which of the observed ionizations (8.88, 10.14 eV) corresponds to the perturbed phosphorus AO(p) and which to the perturbed b_1 MO?

In the case of **1**, where the situation is similar to that in **2**, it has been shown unambiguously that I_1 corresponds to the b_1 π ionization and I_3 to the lone pair.[1,3] Since the lone pair ionization energies of analogous amines and phosphines are similar (Table I), it would seem natural to assume that similar assignments hold for **1** and **2**. Nevertheless Debies and Rabalais[4] have concluded from a study of **2**, diphenylphosphine (**3**), and triphenylphosphine (**4**) that this is not the case, I_1 in **2** corresponding to ionization from the phosphorus lone pair AO(p) and I_3 from the b_1 π MO.

This point needs to be resolved because the chemistry of trivalent phosphorus is determined largely by the availability of the phosphorus lone pair electrons for bonding, which in turn is largely determined by the corresponding ionization energy. Since the arguments put forward by Debies and Rabalais did not seem to us conclusive, we decided to reinvestigate the matter, using a procedure which we hoped would establish the assignments for **2** beyond doubt.

Experimental Section

***p*-Phenylenediphosphine (5).** The diGrignard reagent from p-dibromobenzene reacted with bis(diethylamino)chlorophosphine,[8] following Schindlbauer,[9] to form p-phenylenebis(diethylamino)diphosphine (**6a**). Chlorination of **6a** gave p-phenylenebis(dichlorophosphine) (**6b**) which was reduced[10] with lithium aluminum hydride to **5**, mp 68–70 °C (lit.[10] 69–70.5 °C). The structure and purity of **5** were checked by proton NMR.

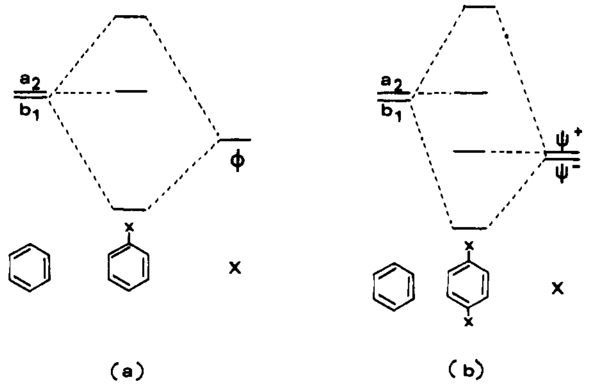


Figure 2. Orbital interaction diagram for (a) C_6H_5X and (b) p-$C_6H_4X_2$.

UPE spectra were acquired on a Perkin-Elmer Model PS-18 photoelectron spectrometer using a He I source (21.22 eV) and, when necessary, a direct inlet heated probe. Calibration and linearity were checked by using argon (15.759-eV line) and xenon (12.130-eV line) as internal standards. The resolution before introducing the sample was in all cases 20–30 meV. The PH_2 group had, however, an unfortunate tendency to degrade the resolution in a time-dependent and reversible manner, leading to a real resolution of 30–60 meV over the range of interest. All quoted ionization values are for band maxima unless otherwise indicated.

MNDO calculations were carried out by using standard MNDO procedures and parameters.[11] All geometries were determined by minimizing the energy with respect to all geometrical variables, no assumptions being made, and using the DFP procedure standard in our MNDO program.[11]

Results

UPE spectra for the compounds discussed here are shown as supplementary material in the microfilm version. The values derived from our spectra, for ionizations in the region below 11 eV, are listed in Table II. Note that our values for **2** (8.88, 9.37, 10.14 eV) differ very significantly from those reported previously[4] (9.18, 9.66, 10.32 eV). The measurements described here were carried out with careful calibration and were completely reproducible, different values for the ionization energies differing by less than 0.03 eV.

Discussion

The crucial experiment by which we hoped to establish unambiguously the assignment of the ionizations in **2** was based on an idea which was by no means new and has indeed been used in a number of similar connections, though not in this particular one.

Consider a para-disubstituted benzene derivative, $C_6H_4X_2$, where each of the groups X has a p or π orbital (ϕ_1 or ϕ_2) that can interact with the benzene π MOs (Figure 2). The substituents may also influence the energies of the benzene π MOs (a_2 and b_1) by field/inductive effects or conjugation involving orbitals of X other than ϕ_1 or ϕ_2; equally, the phenyl group may likewise

---

(8) Chantrall, P. G.; Pearce, C. A.; Toyer, C. R.; Twaits, R. *J. Appl. Chem.* **1964**, *14*, 563.

(9) Schindlbauer, H. *Monatsch. Chem.* **1965**, *96* (6), 1936.

(10) (a) Taylor, R. C.; Kolodny, R.; Walters, D. B. *Synth. Inorg. Met-al-Org. Chem.* **1973**, *3* (2), 175. (b) Schindlbauer, H. *Chem. Ber.* **1967**, *100*, 3432. (c) Maier, L. *Phosphorus* **1974**, *4* (1), 41.

(11) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907. (b) Dewar, M. J. S.; Rzepa, H. S. *Ibid.* **1978**, *100*, 58. (c) Dewar, M. J. S.; Rzepa, H.; McKee, M. L. *Ibid.* **1978**, *100*, 3607.

Table II. Observed (Calculated[a]) Ionization Energies (eV)

compd	I_1	I_2	I_3	I_4	I_5
2	8.88 (9.40)	9.37 (9.58)	10.14 (11.17)		
5	8.78 (9.43)	9.48 (9.73)	9.80 (10.87)	10.30 (11.17)	
1	8.04[b]	9.11[b]	10.70[b]		
7	7.34	9.10	9.71	11.54	
8a	7.5	8.1	8.5	8.8	9.3
8b	(10.02)[d]	(10.21)[d]	(11.26)[d]		
6b	(10.49)[d]	(10.90)[d]	(11.56)[d]	(11.74)[d]	

[a] Calculated by MNDO. [b] Baker, A. D.; May, D. P.; Turner, D. W. *J. Chem. Soc. B* 1968, 22. [c] Slightly different values (7.34, 9.10, 9.71, 11.54) have been reported by: Streets, D. C.; Hall, W. E.; Ceasar, G. P. *Chem. Phys. Lett.* 1972, *17*, 90. [d] Calculated (MNDO) values only. For UPE spectra, see supplementary material.

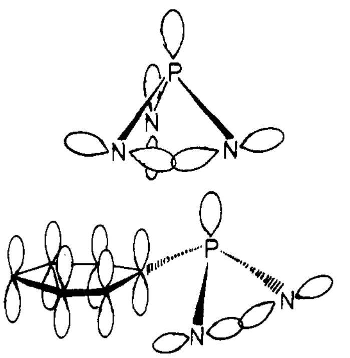


Figure 3. Geometries and orbital interactions in (a) 11 and (b) **8a**.

influence the energies of ϕ_1 and ϕ_2 by processes other than a conjugative interaction with a_2 or b_1. We will take as the zeroth approximation in our perturbation (PMO) treatment a model in which all these secondary effects have been taken into account, i.e., all except the conjugative interactions between ϕ_1 or ϕ_2 and a_2 or b_1.

Since the a_2 MO of the ring has nodes at the points of attachment (1,4) of the substituents in both C_6H_5X and p-$C_6H_4X_2$ (Figure 1), it cannot interact with either ϕ_1 or ϕ_2. Furthermore, since p-$C_6H_4X_2$ has a plane of symmetry σ bisecting the line joining the groups X (Figure 1), ϕ_1 and ϕ_2 can enter only in the symmetry combinations ψ^+ [$= 2^{-1/2}(\phi_1 + \phi_2)$] and ψ^- [$= 2^{-1/2}(\phi_1 - \phi_2)$], the former being symmetric and the latter antisymmetric, for reflection in this plane. Since the b_1 MO is antisymmetric for reflection in σ (Figure 2), it can interact only with ψ^-. Thus ψ^+ should survive unchanged in p-$C_6H_4X_2$. Furthermore, since the groups X are too far apart to influence one another, the orbital energy of ψ^+ in p-$C_6H_4X_2$ should be the same as that of the single X orbital (ϕ) in the unperturbed monosubstituted derivative C_6H_5X. According to Koopmans' theorem,[12] the UPE spectrum of $C_6H_4X_2$ should then show four bands in the low-energy region, two corresponding to the unperturbed a_2 and ψ^+ orbitals and two to the orbitals arising from the interaction between b_1 and ψ^-. Since the interaction cannot lead to an orbital crossing, it must correspond to an orbital of the same type as I_2 (i.e., the pair a_2/b_1 or the pair ψ^+/ψ^-) and I_3 must likewise correspond to an orbital of the same kind as I_4.

The secondary interactions between X and the ring should be additive. The orbital energy of b_1 in C_6H_5X should therefore be the mean of the values for benzene and $C_6H_4X_2$. The same should be true of the energies of the unperturbed X orbitals in C_6H_4X and $C_6H_4X_2$. The UPE spectrum of C_6H_5X will then provide a check on our assignments, because the difference between the energy of the perturbed X orbital (ϕ) and that of ψ^+ in $C_6H_4X_2$ should be equal to the difference between the perturbed and unperturbed energies of b_1. These relationships are indicated in Figure 2.

While the phosphorus lone pair AO in **2** is a hybrid AO, not a pure p AO, we can apply the same arguments to the conjugative interactions between phosphorus and the ring in **2** and p-phenylenediphosphine (**5**). We know that I_2 in **1** (9.37 eV) corresponds to ionization from the a_2 MO, and the corresponding ionization energy in benzene is 9.24 eV. The ionization energy corresponding to the a_2 orbital in **5** should then be 9.37 + (9.37 - 9.24) = 9.50 eV, agreeing almost exactly with the observed value for I_2 (9.48 eV). Since the interaction between the ψ^- and b_1 orbitals in **5** cannot lead to an orbital crossing, the ionization corresponding to ψ^+ must be represented by I_2 or I_3. Since I_2 has been assigned to a_2, the unperturbed lone pair ionization must correspond to I_3 (= 9.80 eV). The perturbation to the ψ^- lone pair orbital in **5** is then equal to $I_4 - I_3$ = 0.50 eV. The energy of the unperturbed b_1 orbital in **5** should then be I_1 + 0.50 = 9.28 eV, leading to an estimate of 9.26 eV for the unperturbed b_1 MO in **1**. If our assignments are correct, the perturbation to the b_1 MO in **1** (i.e., 9.26 - 8.88 = 0.38 eV) should be the same as that to the lone pair AO (i.e., 10.30 - 9.80 = 0.50 eV). The agreement is certainly acceptable, corresponding to errors in the individual IPs of only a few hundredths of an eV. Our assignments are therefore self-consistent. They lead to the conclusion that I_1 in **2** and **5** corresponds in each case to ionization from a perturbed benzene π MO, not from a perturbed lone pair as Debies and Rabalais[4] had claimed. The lone pair ionizations correspond to I_3 in **2** and to I_3 and I_4 in **5**.

Our arguments can be further checked in four ways.

(1) If I_1 in **5** corresponds to the perturbed lone pair orbital, ψ^-, I_3 cannot correspond to ψ^+, because if it did, the perturbation to its energy would be 1.02 eV, leading to an estimated energy for the unperturbed b_1 orbital of 10.30 - 1.02 = 9.28 eV. The interaction between b_1 and ψ^- would then involve an orbital crossing, which is impossible. On the other hand, if I_3 in **5** corresponded to a_2, it would be difficult to explain why its value (9.80 eV) is so much greater than in benzene (9.24 eV), given that the difference between the a_2 ionizations in benzene and **2** is only 0.13 eV.

(2) MNDO has proved surprisingly effective for the calculation of vertical ionization energies of organic molecules using Koopmans' theorem,[12] all the ionizations up to ca. 18 eV[14] being reproduced with reasonable accuracy and almost always in the right order.[11,15] In this connection MNDO has proved superior to any current ab initio method that can be applied to any but very simple molecules. Calculations for a wide variety of phosphorus compounds have shown that the ionization energies of orbitals composed largely of phosphorus AOs are systematically overestimated[16] by ca. 1 eV, but if a corresponding correction is made, the results again agree with experiment to within a few tenths of an eV.[15] Table II includes uncorrected values calculated in

---

(12) Koopmans, T. *Physica* (*The Hague*) **1931**, *1*, 41.

(13) The two changes remain equal only if overlap is neglected. If it is included, the change in the energy of the larger of the two orbital energies is less than that in the smaller. However, the difference remains small so long as the perturbations are small and the success[2] of the simple treatment suggests that this should be true for the cases considered here.

(14) The energies of MOs composed largely of 2s AOs are overestimated by MNDO as a result of the neglect of 1s–2s interactions.

(15) For some further examples, see: Dewar, M. J. S.; McKee, M. L.; *Inorg. Chem.* **1978**, *17*, 1075. Dewar, M. J. S.; Ford, G. P.; Rzepa, H. S. *Chem. Phys. Lett.* **1977**, *50*, 262. The results for all the molecules calculated in ref 11 showed a similar agreement with experiment.

(16) The error arises from neglect of interactions between the phosphorus AOs (both 3s and 3p) with orbitals of the core (1s,2s,2p); see ref 14. Calculations for a number of phosphorus compounds will be presented in a forthcoming paper reporting the parametrization of MNDO for phosphorus.

this way for **2** and **5**. In each case, the calculated order agrees with that deduced above, I_1 and I_2 corresponding to the benzene π MOs and I_3 and I_4 to phosphorus lone pairs. The values for the latter are, as expected, ca. 1 eV greater than those observed. Note also that the values for the perturbed b_1 orbitals (i.e., I_1) are also too large, the errors being greater than usual for MNDO and much greater than for I_2 (which corresponds in each case to the unperturbed a_2 MO). This again is to be expected because the interaction between the b_1 and ψ^- orbitals mixes them together, so I_1 now corresponds to ionization from an orbital composed to a significant extent of a phosphorus AO.

(3) We have already noted the close correspondence between the lone pair ionization energies of analogous compounds of nitrogen and trivalent phosphorus (Table I). This suggests that the assignments in **2** and **5** should follow the same pattern as in their nitrogen analogues, aniline (**1**) and *p*-phenylenediamine (**7**). The UPE spectra of the latter have been assigned unambiguously,[17] I_1 and I_2 corresponding to the benzene π MOs, not to phosphorus lone pairs. As expected, this corresponds to the assignments we arrived at above for **2** and **5**.

(4) The arguments used in assigning the spectra of **2** and **5** can be further tested by applying them to the nitrogen analogues **1** and **7**. The necessary data are shown in Table II. I_2 in **1** must correspond to the a_2 π MO. Since the values of I_2 in **1** and **7** are the same (9.11, 9.10 eV), I_2 in **7** must also correspond to ionization from the unperturbed a_2 MO. I_3 in **7** (9.71 eV) must then correspond to the unperturbed nitrogen lone pair. The energy of the unperturbed nitrogen lone pair AO in **1** should then also be 9.71 eV. Since this lies below the energy of the b_1 π MO, I_3 in **1** must correspond to the perturbed lone pair and I_1 to the perturbed b_1 π MO. Assuming the unperturbed energies of the a_2 and b_1 π MOs to be the same (9.11 eV), the perturbations to the b_1 π MO and the lone pair are, respectively, $9.11 - 8.04 = 1.07$ eV and $10.70 - 9.71 = 0.99$ eV. These are almost the same, as our simple perturbation treatment requires. The same is true of the perturbations in **7**, to the b_1 π MO ($9.10 - 7.34 = 1.76$ eV) and the lone pair ($11.54 - 9.71 = 1.83$ eV). The treatment is thus self-consistent and it leads of course to the established[1,3] assignments for both compounds.

Table II also shows ionization energies calculated for **1** and **7**, using MNDO and Koopmans' theorem. The order of orbital energies is correctly reproduced, I_1 and I_2 corresponding to π MOs. The calculated values agree well with experiment, the differences being well within the error limits for MNDO.

Since our synthetic routes to **2** and **5** involved the corresponding bis(diethylamino)phosphines, **6a** and **8a**, and the dichlorophosphines, **6b** and **8b**, as intermediates, we also measured their UPE spectra; see Table II.

In the case of **6b** and **8b**, the ionizations coalesce into a single, poorly resolved band. Evidently the conjugative interaction between PCl_2 and the ring must be minimal. The benzene π ionizations are shifted to higher energies by the field/inductive effects of the PCl_2 group(s). The phosphorus lone pair ionization energies must be close to the value (9.80 eV) estimated above for the energy of an unperturbed phosphorus lone pair orbital in **1** or **5**. This would be expected in view of the close parallel between the phosphorus lone pair ionization energies in PH_3 and PCl_3 (Table I).

MNDO calculations for **6b** and **8b** confirmed these conclusions in an interesting manner. In both cases the PCl_2 group is predicted to adopt a conformation (see **9**, **10**) in which the plane of the ring bisects the ClPCl angle, the phosphorus lone pair orbitals being consequently orthogonal to the π MOs of the ring. The calculated ionization energies (Table II) agree reasonably well with experiment. If a correction of 1 eV is applied to the values for the lone pairs, all the lower ionization energies of **1** and **5** are predicted in each case to lie within a few tenths of an eV.

The situation in **6a** and **8a** is more complicated because here the nitrogen lone pairs should also have ionizations in the low-energy region. The UPE spectrum of **8a** should show five low-energy ionizations, that of **6a** no less than eight. The spectrum of **8a**, while poorly resolved, does indeed show five distinct bands in the region below 10.5 eV; that of **8a**, however, is not resolved. We cannot therefore use our procedure to assign the various ionizations. Nevertheless a plausible interpretation of the UPE spectrum of **8a** can be obtained by comparing it with that[18] of tris(dimethylamino)phosphine (**11**).

Lone pair repulsions, combined with steric effects, force two of the amino groups in **11** to orient themselves with their lone pair orbitals (n_1 and n_2) orthogonal to the phosphorus lone pair orbital (p), the latter interacting with the lone pair orbital (n_3) of the third amino group (Figure 3a). Steric effects force n_1 and n_2 to interact in spite of the resulting repulsion between them, leading to a splitting by ±0.6 eV. Analogy suggests that **8a** will adopt a similar configuration (Figure 3b) with phenyl replacing the third amino and with the b_1 MO replacing n_3. Since ethyl is more strongly electron releasing than methyl, the unperturbed nitrogen lone pair ionization energy in **8a** should be less than in **11** (8.23 eV[18]). Since phenyl is smaller than NEt_2, the nitrogen lone pairs in **8a** should be able to avoid each other better than in the case of **11**, leading to a smaller splitting. On this basis we can assign I_1 (7.5 eV) and I_2 (8.1 eV) to the nitrogen lone pairs, I_4 (8.8 eV) to the unperturbed a_2 MO, I_3 (8.5 eV) to the perturbed b_1 MO, and I_5 (9.3 eV) to the phosphorus lone pair. The interaction between b_1 and p changes the energy of the former by 0.3 eV, the same as in **1**, as might be expected. The unperturbed phosphorus lone pair energy in **8a** is then $9.3 - 0.3 = 9.0$ eV. This is less by 0.6 eV than the value in **11**.[18] It seems unlikely that it could be any lower, as would be required by any assignment other than the one given here.

Conclusions

(1) The work reported here provides very strong evidence for a revised assignment of the ionizations in phenylphosphine (**1**), I_1 corresponding to ionization from a perturbed benzene (b_1) π MO and I_3 to the unperturbed phosphorus lone pairs (p).

(2) Conjugation between PCl_2 and the ring in phenyldichlorophosphine (**8b**) or *p*-phenylenebis(dichlorophosphine) (**6b**) seems to be unimportant. Indeed, it seems likely that both molecules have C_{2v} symmetry, the lone pair AO of each PCl_2 group lying in the plane of the ring.

(3) The UPE spectrum of phenylbis(diethylamino)phosphine (**8a**) has been tentatively assigned by comparing it with that of tris(dimethylyamino)phosphine (**11**).

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008), the Robert A. Welch Foundation (Grant F-126 and F-135), and the National Science Foundation (Grant CHE-79-10155). The calculations were carried out on the CDC 6400/6600 computer at The University of Texas Computation Center. We also thank Dr. Michael Lattman for his help.

Supplementary Material Available: UPE spectra for (a) **2**, (b) **5**, (c) **8a**, (d) **6a**, (e) **8b**, and (f) **6b** (7 pages). Ordering information is given on any current masthead page.

---

[17] See: Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; Wiley: New York, 1977.

[18] Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Schweiger, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 6506.