(21) W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, **94**, 6853 (1972).
(22) A. L. J. Beckwith and J. E. Goodrich, *Aust. J. Chem.*, **18**, 747 (1965).
(23) R. S. Neale, N. L. Marcus, and R. G. Shepers, *J. Am. Chem. Soc.*, **88**, 3051 (1966).
(24) Y. L. Chow and T. C. Joseph, *Chem. Commun.*, 490 (1969).
(25) Y. L. Chow, N. S. Tam, and A. C. H. Lee, *Can. J. Chem.*, **47**, 2441 (1969).
(26) O. E. Edwards, J. M. Paton, M. H. Benn, R. E. Mitchell, C. Watanada, and K. W. Vohra, *Can. J. Chem.*, **49**, 1648 (1971).
(27) F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 2767 (1955).
(28) It may be noted that acylation of 2-azatricyclo[2.2.2.$0^{2,6}$]octane yields instead predominantly bicyclo[2.2.2]amides.[29]
(29) W. Nagata, S. Hirai, K. Kawata, and T. Aoki, *J. Am. Chem. Soc.*, **89**, 5045, 5046 (1967).
(30) These compounds were obtained from Diels-Alder addition of acrylic acid to isoprene, separation of the resultant acids,[31] and subsequent conversions to the chloroamides.
(31) A. Manjarrex, T. Rios, and A. Guzman, *Tetrahedron*, **20**, 333 (1964).
(32) F. B. LaForge, N. Green, and W. A. Gersdorff, *J. Am. Chem. Soc.*, **70**, 3707 (1948).
(33) M. Mousseron and F. Winternitz, *Bull. Soc. Chim. Fr.*, 604 (1946).
(34) C. Wolff, *Justus Liebigs Ann. Chem.*, **201**, 45 (1880).
(35) H. Machleidt, *Justus Liebigs Ann. Chem.*, **667**, 24 (1963).
(36) W. Schneider and M. Muller, *Arch. Pharm.* (*Weinheim*), **294**, 360 (1961).

Ultraviolet Photoelectron Spectra of Some Substituted Triarylphosphines

Michael A. Weiner* and Michael Lattman

Department of Chemistry, The City College of The City University of New York, New York, New York 10031

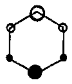
Samuel O. Grim

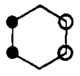
Department of Chemistry, University of Maryland, College Park, Maryland 20742

Received September 30, 1974

The photoelectron spectra of a series of triarylphosphines, containing various ring substituents, have been investigated. The spectra show a band due to ionization from the phosphorus lone pair (IP_1), followed by one or more bands assigned to ionizations of the phenyl π electrons. The values of IP_1 are sensitive to the nature of the ring substituents and reflect the influence of the substituents on the charge density at the ring position adjacent to the phosphorus. The number of observed IP's in the region assigned to the phenyl π electrons are generally the same as the number of IP's for the corresponding monosubstituted benzene. Moreover the IP values are generally close to the IP's found for the monosubstituted benzenes. The observed results are explained by a lack of substantial resonance interaction between the phosphorus and the π orbitals of the aryl system. The variation of phosphorus lone pair IP values is discussed in terms of charge stabilization in the radical cation produced by ionization of a lone-pair electron.

Several recent articles on the ultraviolet photoelectron spectra (pes) of monosubstituted benzenes have discussed the effect of substitution on ionization from the $e_g\pi$ orbitals of benzene.[1-7] The resonance effect of certain substituents (OR,[3] CH_3[4,7]) on the b_1 orbital[8] appears to raise its energy (lower ionization potential) from that of the a_2 orbital,[8] and thus the first ionization potential (IP) can be assigned to ionization from the b_1 orbital. The second ionization is then from the a_2 orbital and appears unchanged from the corresponding ionization in benzene (9.24 eV). Other substituents (F,[4] Cl[6]) show the same resonance effect, but an electron-withdrawing inductive effect is apparently also present. Thus the first two IP's are assigned as before, but the IP values are somewhat larger. In monosubstituted benzenes containing a third class of substituents (*tert*-butyl,[9] $(CH_3)_3Si$,[9] CF_3[9]) the ionizations from the a_2 and b_1 orbitals are close in energy and are either poorly resolved or not at all. The band envelopes are raised or lowered in energy from that of benzene, depending on whether the substituent is electron donating or withdrawing.


b_1


a_2

In the present study we have investigated the pes of a series of triarylphosphines containing these ring substituents. Schäfer and Schweig[10] have interpreted the pes of dimethylphenylphosphine in terms of a complete lack of interaction between the aryl group and the trivalent phosphorus atom. The energies of ionization from the phosphorus lone pair and phenyl π orbitals remain virtually the same as in $(CH_3)_3P$ and benzene, respectively. Debies and Rabalais[11] observed in the pes of $C_6H_5PH_2$ a stabilization of the phenyl π orbitals and a splitting of the a_2 and b_1 components, along with a destabilization of the phosphorus lone pair. It was suggested that this is due to delocalization of charge from phenyl π orbitals into the d orbitals on phosphorus. (The IP of the phenyl π electrons in $(C_6H_5)_3P$ is the same as in benzene, however, and no splitting of the components was observed.)

Results and Discussion

The pes of the substituted triarylphosphines (Table I) show one or more peaks in the region assigned to ionization of the phenyl π electrons in the corresponding monosubstituted benzenes (Table II). In most cases the number of IP's observed in this region corresponds to the number of IP's observed for the monosubstituted benzene. In addition to these, a low IP band is observed in each of the spectra, which is readily assigned, as by the previous authors,[10,11] to ionization from the lone pair of electrons on phosphorus.

Although the complexity of the molecules studied appears to inhibit the use of vibrational fine structure in assigning the bands in the phenyl region, it seems likely that the band assignments for the triarylphosphines generally correspond to the assignments made for the monosubstituted benzenes. The following reasons are apparent.

(1) In almost all cases, and independent of the nature of the substituent, the IP's assigned to the phenyl electrons in $aryl_3P$ correspond closely to the IP's found for the monosubstituted benzene. Particularly in the case of $aryl_3P$ substituted with methoxy and dimethylamino groups, the separation of ionizations from the a_2 and b_1 orbitals is so large that it is unlikely that the assignments could be reversed upon substitution into the phosphino system, with one energy level raised and the other lowered from the value in the monosubstituted benzene.

Table I
Vertical Ionization Potentials[a] of $(RC_6H_4)_3P$

Compd	R	IP_1[b]	IP_2[c]	IP_3[c]	IP_4
1	4-CF_3	8.65	9.8^{d}	9.9	
2	4-Cl	8.18	9.16	9.63	11.40^{e}
3	4-F	8.12	9.6^{f}		
4	4-H	7.92	9.20		
5	4-$(CH_3)_3Si$	7.67	8.84	9.02	
6	4-CH_3	7.6	8.9^{f}		
7	4-$(CH_3)_2CH$	7.53			
8	4-$(CH_3)_3C$	7.52	8.8^{f}		
9	4-CH_3O	7.48	8.30	9.00	
10	4-$(CH_3)_2N$	$6.9–7.0^{d}$	7.30^{g}	8.67	9.56^{h}
11	2-CF_3	8.30	9.5^{d}	9.68	
12	2-CH_3	7.64	8.62	9.4^{d}	
13	2-CH_3O	7.37	8.22	8.71	
14	3-F	8.32	9.2	$9.6–9.7^{d}$	
15	3-CH_3	7.68	8.58	9.53	
16	3-CH_3O	7.72	8.35	9.03	

[a] In electron volts. [b] Phosphorus lone pair. [c] Phenyl π electrons. [d] Shoulder. [e] Chlorine lone pair. This band is accompanied by a shoulder at 11.7 eV, also assigned to a chlorine lone pair. [f] IP_2 and IP_3 are unresolved. The value listed is the maximum of the resulting peak. [g] Ionization apparently from $(CH_3)_2N$ lone pair. [h] Assigned to an ionization from a phenyl π orbital.

Table II
Vertical Ionization Potentials[a] of RC_6H_5

Registry no.	R	IP_1[b]	IP_2[b]	IP_3[b]
98-08-8	CF_3^{c}	9.7		
462-06-6	F^{d}	9.11(b_1)	9.82(a_2)	
108-90-7	$Cl^{c,e}$	9.1(b_1)	9.7(a_2)	11.32^{f}
71-43-2	H	9.24		
768-32-1	$(CH_3)_3Si^{c}$	9.0^{g}	$9,3^{g}$	
108-88-3	CH_3^{d}	8.72(b_1)	9.24(a_2)	
98-06-6	$(CH_3)_3C^{c}$	9.0		
100-66-3	CH_3O^{h}	8.42(b_1)	9.21(a_2)	
121-69-7	$(CH_3)_2N^{h}$	7.45(b_1)^{i}	9.00(a_2)	9.85(b_1)

[a] In electron volts. [b] Assignments in parentheses. [c] Reference 9. [d] Reference 4. [e] Reference 6. [f] Chlorine lone pair. Accompanied by a band at 11.7 eV also assigned to a chlorine lone pair. [g] Two components of the band envelope were attributed to IP_1 and IP_2 by R. A. N. McLean, *Can. J. Chem.*, 51, 2089 (1973). [h] Reference 3. [i] Ionization apparently correlates with $(CH_3)_2N$ lone pair.

(2) There is no great change in the phenyl IP values among the ortho, meta, or para isomers with a given substituent. The effect of substitution into the phosphino system on the relative a_2 and b_1 IP's would be expected to vary with the position of substitution.

(3) In the $aryl_3P$ containing CF_3, $(CH_3)_3C$, and $(CH_3)_3Si$ substituents, the ionizations from the a_2 and b_1 phenyl orbitals are not resolved. This is also true for the corresponding substituted benzenes. Therefore there is no evidence here that the relative energies of the a_2 and b_1 orbitals are changing much upon substitution into the phosphino system.

The phosphorus lone pair IP values appear to be a well-behaved function of the electron-donating or -withdrawing nature of the substituents. A very good correlation (correlation coefficient 0.986) is observed between the Hammett σ_p parameter[12] and the lone pair IP of phosphorus (see Figure 1) for the ten compounds with para substituents. The inductive electron-withdrawing nature of the fluorine and chlorine atoms is indicated, but the effect is apparently partially cancelled in the para derivatives by the electron-donating resonance effect, which places charge on the ring position adjacent to the phosphorus, and causes some lowering of the lone pair IP. In the *m*-fluoro derivative the resonance effect is submerged, and the result is a noticeable raising of the phosphorus lone pair IP. The strong resonance effect of the *p*-dimethylamino and *p*-methoxy substituents enhances the electron density adjacent to the phosphorus, and the result is a pronounced lowering of the IP value, whereas the somewhat higher value for the *m*-methoxy derivative is consistent with the diminished resonance effect at the meta ring position. The electron-donating effect of the alkyl groups is expected, but the lack of any change in the lone pair IP's among the ortho, meta, and para methyl derivatives should be noted. Despite the inductive effect of the $(CH_3)_3Si$ group, it appears to be only a modest electron donor, poorer than the alkyl groups. This phenomenon is well documented[13] and is believed to be due to an electron-withdrawing component in the behavior of the silicon, in which charge from the aromatic ring is delocalized into the dπ orbitals of the silicon.

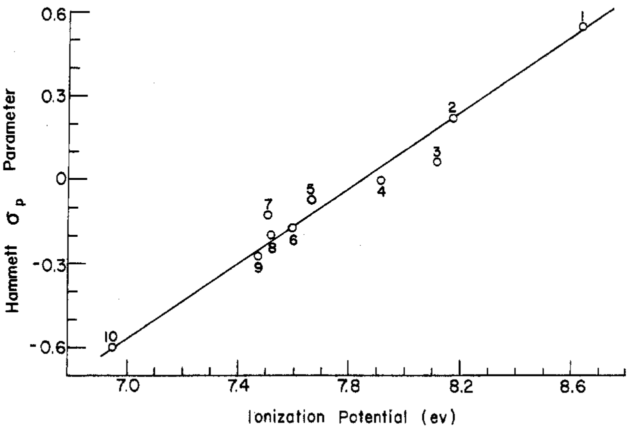


Figure 1. Correlation of ionization potential of the phosphorus lone pair with the Hammett σ_p substituent constant for $(p\text{-}RC_6H_4)_3P$. The numbers on the points correspond with the compound numbers in Table I.

The results of this study show that while the effect of the substituted aryl groups on the phosphorus lone pair electrons is easily rationalized, there is little apparent effect of the phosphorus on the π orbital energies of the aryl system. This observation is independent of the nature of the aryl substituent. This would appear to rule out any substantial resonance effect between the phosphorus lone pair of electrons and the filled π orbitals of the ring, or any substantial stabilization of the phenyl π orbitals by interaction with the phosphorus d orbitals. The lack of resonance interaction is consistent with the finding of Schäfer and Schweig.[10] More generally, there is little evidence that the trivalent phosphorus acts as a significant electron donor or acceptor toward an attached aryl group.[14]

It is suggested that the correlation between the phosphorus lone pair IP values and the substituent σ_p values should be discussed in terms of the effect of the substituent on the energy difference between the ground state and the cationic state (analogous to the consideration of σ_p as measuring the effect of the substituent on the energy difference between the ground state and a charged transition state[12]). This effect is determined largely by the action of the substituent on the developing charge at the "reaction site" (here the phosphorus atom). In this case migration of electrons from the substituted aryl groups to the positive phosphorus center would result in a stabilization of the cation. Thus not only would lower lone pair IP's result than those expected from Koopmans' theorem[15] but the magnitude of the charge migration (and therefore lowering of the IP) is related to the σ_p value of the substituent. The lack of deviation from the normal σ_p correlation, particularly on the part of the dimethylamino and methoxy substituents, argues against any enhanced resonance interaction between the substituents and the positive phosphorus center, and therefore the drift of charge would be through the P–aryl σ bond. On the other hand, the ability of the trivalent phosphorus to effect significant stabilization of the radical cation, produced by ionization from the aryl π orbitals, appears to be quite limited.

It should be noted that any correlation between phosphorus lone pair IP's and substituent σ_p values assumes no significant difference in hybridization at the phosphorus among the para-substituted aryl$_3$P. Thus the effects discussed above are not extended here to a comparison between the aryl$_3$P and other phosphines. For instance the lone-pair IP's for PH_3, $(CH_3)_3P$, and $(C_6H_5)_3P$ are 9.9,[9] 8.6,[16] and 7.9 eV, respectively, and this difference appears to reflect the difference in bond angles at the phosphorus (94°,[17] 99°,[18] and 103°,[19] respectively).[20]

Experimental Section

The spectra were obtained with a Perkin-Elmer Model PS-18 photoelectron spectrometer, using the He(I) resonance line (21.22 eV). Since elevated temperatures were necessary for proper sample vapor pressures, a direct inlet probe was used for all samples. Temperatures generally in the range of 60–130° were used in order to obtain proper count rates, but 150° was necessary for the p-$(CH_3)_3C$ and p-$(CH_3)_3Si$ derivatives, and 240° was necessary for the p-$(CH_3)_2N$ compound. The spectra were calibrated with Ar (15.759- and 15.937-eV lines) and Xe (12.130-eV line), used as internal standards. The values listed for IP_1 (Table I) are the band maxima. In order to obtain a comparison between the phenyl IP values for aryl$_3$P and the corresponding monosubstituted benzenes, the values of IP_2 and IP_3 (Table I) were obtained as often as possible in accordance with the method of obtaining the vertical IP's for the corresponding monosubstituted benzene (Table II).

The phosphine samples were prepared by the Grignard method.[21]

Acknowledgment. We are grateful to Dr. A. W. Yankowsky, Mr. H. A. Zunger, and Mr. B. Marien for preparation of most of the aryl phosphines. S.O.G. also thanks the National Science Foundation for partial support of this work under Grant No. GP 30703. We thank Professor N. McKelvie for his helpful advice.

Registry No.—**1**, 13406-29-6; **2**, 1159-54-2; **3**, 18437-78-0; **4**, 603-35-0; **5**, 18848-96-9; **6**, 1038-95-9; **7**, 29949-82-4; **8**, 54409-77-7; **9**, 855-38-9; **10**, 1104-21-8; **11**, 25688-42-0; **12**, 6163-58-2; **13**, 4731-65-1; **14**, 23039-94-3; **15**, 6224-63-1; **16**, 29949-84-6.

Supplementary Material Available. Photoelectron spectra of **1–16** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JOC-75-1292.

References and Notes

(1) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

(2) R. A. W. Johnstone and F. A. Mellon, *J. Chem. Soc., Faraday Trans. 2*, **69**, 36 (1973).

(3) J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, **69**, 521 (1973).

(4) T. P. Debies and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 355 (1972).

(5) J. W. Rabalais and R. J. Colton, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 83 (1972).

(6) J. N. Murrell and R. J. Suffolk, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 471 (1972).

(7) M. Klessinger, *Angew. Chem., Int. Ed. Engl.*, **12**, 422 (1973).

(8) The a_2 and b_1 designations are appropriate only for the C_{2v} symmetry of C_6H_5X, but for the sake of simplicity of nomenclature, the same designations will be used for the orbitals which correlate with these in the aryl$_3$P system.

(9) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, New York, N.Y., 1970.

(10) W. Schäfer and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **11**, 836 (1972).

(11) T. P. Debies and J. W. Rabalais, *Inorg. Chem.*, **13**, 308 (1974).

(12) H. H. Jaffe, *Chem. Rev.*, **53**, 222 (1953).

(13) C. J. Attridge, *Organomet. Chem. Rev., Sect. A*, **5**, 323 (1970); E. A. V. Ebsworth in A. G. MacDiarmid, Ed., "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, Marcel Dekker, New York, N.Y., 1968, pp 82–88.

(14) R. Benassi, M. L. Schenetti, F. Taddei, P. Vivarelli, and P. Dembech, *J. Chem. Soc., Perkin Trans. 2*, 1338 (1974).

(15) F. Brogli, P. A. Clark, E. Heilbronner, and M. Neuenschwander, *Angew. Chem., Int. Ed. Engl.*, **12**, 422 (1973); M. A. Weiner and M. Lattman, *Tetrahedron Lett.*, 1709 (1974).

(16) I. Hillier and V. R. Saunders, *Trans. Faraday Soc.*, **66**, 2401 (1970).

(17) H. H. Nielsen, *J. Chem. Phys.*, **20**, 759 (1952).

(18) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

(19) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

(20) We thank a reviewer for pointing out this limitation on our results.

(21) A. W. Yankowsky, Ph.D. Dissertation, University of Maryland, 1970.

Stereochemistry of Dihydrothiophene Formation from Vinylphosphonium Salts[1a]

John M. McIntosh* and Gary M. Masse[1b]

Department of Chemistry, University of Windsor, Windsor, Canada N9B 3P4

Received November 4, 1974

Evidence is presented which shows that the *cis*-2,5-dialkyl-2,5-dihydrothiophenes are formed in preference to the trans isomers in the reaction between vinylphosphonium salts and α-mercaptocarbonyl compounds. Substituent trends suggest a steric basis for this effect. The implications of the results for stereoselective conjugated diene preparation are discussed. Seven new examples of the synthesis of the dihydrothiophenes are reported.

One of the most active areas in organic synthesis in the past decade has been the development of methods for the construction of unsaturated compounds in stereoselective and stereospecific ways. Whereas the preparation of 1,5-dienes is an active field,[2] work on the stereoselective synthesis of 1,4- and 1,3-dienes has been limited. As we have pointed out,[3] this has greatly restricted the application of the Diels–Alder reaction to stereospecific organic synthesis.

One method of 1,3-diene synthesis which has been shown to be stereospecific is the thermal decomposition of 2,5-