

HOC(O)CF₃, 76-05-1; HOC(O)CCl₃, 76-03-9; (H₃GeN:)₂C, 10592-53-7; ((CH₃)₃GeN:)₂C, 30006-65-6; (H₃SiN:)₂C, 4468-88-6; ((CH₃)₃SiN:)₂C, 1000-70-0; H₃GeF, 13537-30-9; CH₃GeH₂F, 30123-02-5; (CH₃)₂GeHF, 34117-35-6; (CH₃)₃GeF, 661-37-0; (CH₃)₃SiCl, 75-77-4; (CH₃)₃SiBr, 2857-97-8; (CH₃)₃SiI, 16029-98-4; (CH₃)₃SiF, 420-56-4; Me₂GeF₂, 811-70-1; Me₂Ge(OC(O)CCl₃)₂, 62600-98-0; Me₂GeFOC(O)CCl₃, 62600-99-1; BF₃, 7637-07-2; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; (CH₃)₂GeHO-C(O)CCl₃, 62601-00-7.

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Photoelectron Spectra of Tris(dialkylaminophosphines). A Controversy

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The photoelectron spectra of tris(dimethylaminophosphine) (I), tris(diethylaminophosphine) (II), and tris(dipropylaminophosphine) (III) have been studied in an effort to resolve a controversy pertaining to the interpretation of the spectrum of I. The current interpretation concludes that I, II, and III have C_3 skeletal symmetry with two nitrogen lone pairs interacting in a σ manner, while the remaining nitrogen lone pair interacts in a π fashion with the phosphorus lone pair. The second and third ionization bands correspond to the phosphorus-nitrogen lone-pair interaction.

Several laboratories recently have been using ultraviolet photoelectron spectroscopy to predict conformational geometries, particularly for molecules containing "lone-pair" electrons.¹ The rapid time scale of the ionization process in photoelectron spectroscopy (Franck-Condon transitions) permits observation of the spectrum of the predominant conformation (or conformations) of a molecule even though low barriers to bond rotations allow rapid equilibration of geometries. This technique therefore avoids the "time-averaged" spectra which complicate the utilization of NMR in conformational analysis studies. This technique is particularly useful in studying compounds having electrons in nonbonding orbitals on adjacent atoms since such orbitals interact to produce symmetric and antisymmetric molecular orbitals if they are oriented in a manner such that the two orbitals are not orthogonal. The magnitude (or presence or absence) of these interactions can therefore be utilized to deduce the conformations of this type of molecule.

Cowley and co-workers² first reported the photoelectron spectrum of tris(dimethylaminophosphine) (I). On the basis primarily of comparison with the spectra of several aminophosphines which contain one or more fluorine atoms, they

concluded that I must have C_3 symmetry with two of the nitrogen lone pairs interacting in a σ fashion, while the remaining N lone pair interacts in a π manner with the phosphorus lone pair. Furthermore, they assigned the first and third ionization bands for I ($I_1 = 7.61$ eV, $I_3 = 8.86$ eV) to correspond to the two interacting sets of N lone pairs, while the second and fourth bands ($I_2 = 7.89$ eV, $I_4 = 9.98$ eV) were attributed to the interacting N and P lone pairs. The authors suggested that an early electron diffraction study³ of I, which was interpreted to indicate that the molecule has a C_3 axis of symmetry, needed to be reinterpreted. Later, Lappert and co-workers⁴ reexamined the photoelectron spectrum of I in connection with a study of several haloaminophosphines. The latter workers criticized the Cowley interpretation and suggested that I has C_{3v} symmetry with all of the N lone pairs interacting in a π fashion with P and with each other. Such an interpretation dictates that bands I_1 and I_4 at 7.30 and 9.80 eV in their spectrum be assigned to the a_1 combination of N and P, while bands I_2 and I_3 at 7.95 and 8.60 eV must be attributed to the Jahn-Teller split ²E ionic state which has no P lone-pair contribution.⁵ Thus, the Cowley interpretation proposes that the highest occupied molecular orbital for I

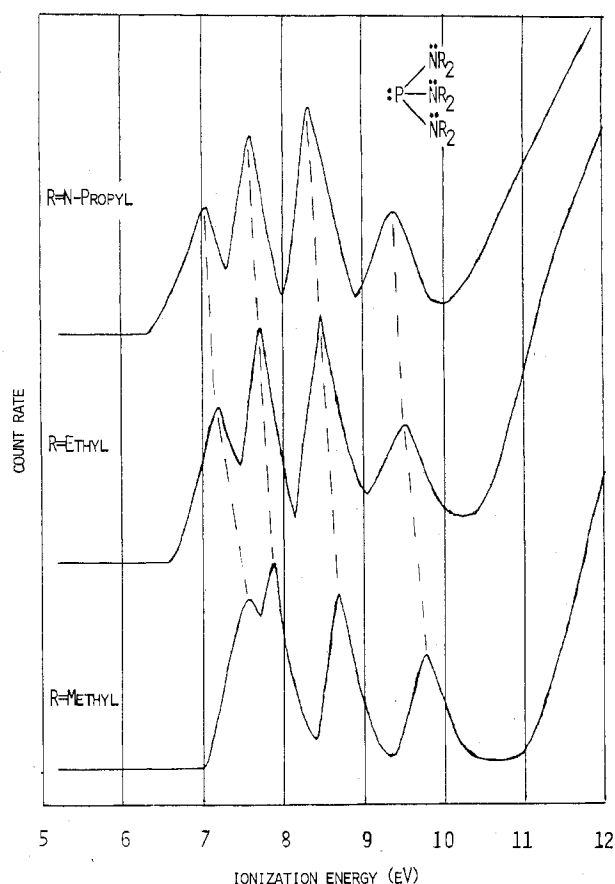


Figure 1. Photoelectron spectra of three tris(dialkylaminophosphine). Excitation source was the He I resonance line.

contains no contribution due to the P lone pair, while the Lappert interpretation contends that the HOMO does involve the P lone pair.

This paper will offer an alternative interpretation of the spectrum of I based upon new data obtained from the photoelectron spectra of tris(diethylaminophosphine), II, and tris(dipropylaminophosphine), III.

Experimental Section

Materials. Tris(dimethylaminophosphine), I, was purchased from Aldrich and purified by collecting a sample by gas chromatography using a 10 ft \times $1/4$ in. 20% SE 30 on Chromosorb W column. Tris(diethylaminophosphine) and tris(di-*n*-propylaminophosphine), II and III, were prepared by standard methods⁶ and purified as described above. All compounds gave satisfactory mass spectra and ¹³C and ¹H NMR spectra.

Photoelectron Spectra. All photoelectron spectra in this work were obtained on a Perkin-Elmer PS 18 spectrometer using the He I resonance line as an excitation source. The samples were sufficiently volatile so that they could be studied at room temperature. At least five spectra were measured for each compound, and the data to be presented in this paper represent an average of those for all runs. Argon and xenon were employed as internal calibrants in all of the runs. The resolution of the spectrometer was ca. 30 mV throughout this study.

Results

The photoelectron spectra for the dialkylaminophosphines studied in this work are depicted in Figure 1; the inert-gas calibration lines have been omitted from the figure. The vertical ionization potentials measured from the spectra are given in Table I. Table I also contains the vertical ionization potentials for I which were reported by Cowley and co-workers² and by Lappert and co-workers.⁴ The usual error attributed to deducing vertical ionization potentials from well-resolved photoelectron spectra is 0.01–0.05 eV.⁷ The three

Table I. Lone-Pair Ionization Energies of Some Tris(dialkylaminophosphines)^a

Compd	Ref	I_1	I_2	I_3	I_4
P[N(CH ₃) ₂] ₃	Cowley et al. ²	7.61	7.89	8.86	9.98
	Lappert et al. ⁴	7.30	7.95	8.60	9.80
	This work (I)	7.59	7.91	8.75	9.89
P[N(CH ₂ CH ₃) ₂] ₃	This work (II)	7.19	7.68	8.46	9.48
P[N(CH ₂ CH ₂ CH ₃) ₂] ₃	This work (III)	7.05	7.58	8.34	9.33

^a All ionization energies are in eV.

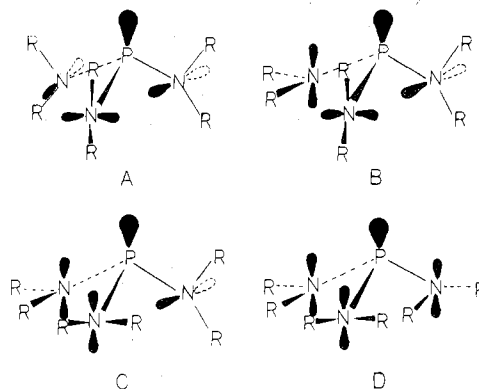


Figure 2. Possible structural models for the tris(dialkylaminophosphines).

sets of data in Table I for compound I do not conform to this expectation, for the I_1 values alone span a range of 0.31 eV. Since the instruments used in the three laboratories are basically the same, the rather wide range of values must be attributed to the means by which each laboratory chooses the vertical ionization potential. Our method has been discussed previously.⁸

The photoelectron spectra of I–III possess four well-resolved bands in the 7–10-eV region, all of which can be attributed to removal of electrons which are primarily in orbitals non-bonding in nature. Figure 1 shows that the three spectra are quite similar in pattern, although the spacing between the bands changes upon progression from I to III. It is evident that in interpreting the three spectra, the same basic structural model should be applicable.

Discussion

All four of the lone-pair ionization bands decrease in ionization energy in the series I to II to III. This, of course, is due to the tendency of an alkyl group to serve as an electron donor in stabilizing the various ionic states; the efficiency of such a stabilization process always increases with increasing chain length of the alkyl group.⁷ The first and fourth ionization bands (I_1 and I_4) are stabilized to a greater extent (ca. 0.40 eV), upon progressing from compound I to II, than are the second (0.23 eV) and third (0.29 eV) bands. A reasonable inference here is that the phosphorus lone pair should be associated with I_2 and I_3 since the stabilizing alkyl groups are directly bonded to the nitrogen atoms rather than to phosphorus. Therefore, a new interpretation of the photoelectron spectrum of I which is different than either of the previous ones^{2,4} is warranted.

In interpreting the spectra of I–III, we have considered numerous possible structural models, four of which are shown in Figure 2. Model A possesses C_{3v} local symmetry with all of the nitrogen lone pairs orthogonal to the phosphorus lone pair. In all of the models the N's are considered to be sp^2 hybridized, and the P is considered to be sp^3 hybridized, as suggested by Viličkov and co-workers³ in their electron diffraction study. The local symmetry of model B is C_3 with two of the N lone pairs orthogonal to the remaining N lone pair and the P lone pair. This model was employed by Cowley

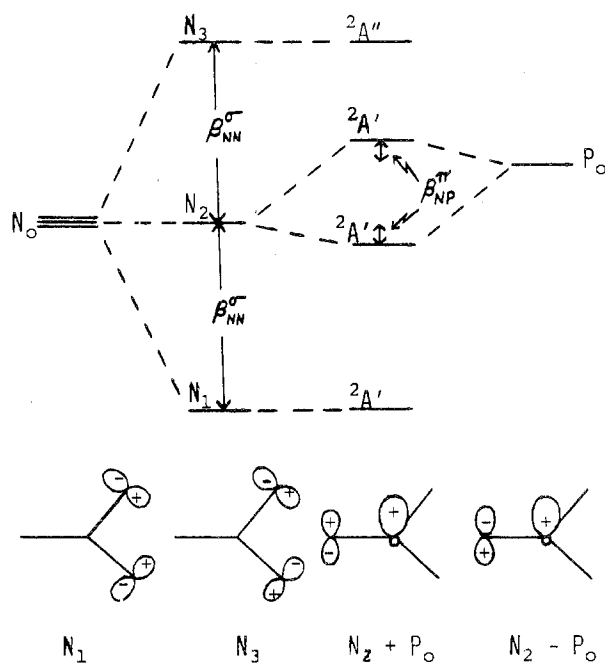


Figure 3. Possible energy level diagram for structural model B which would explain the observed photoelectron spectra of the tris(dialkylaminophosphines).

and co-workers² in their interpretation of the spectrum of I. Model C possesses C_3 local symmetry also, but in this case only one N lone pair is orthogonal to the P lone pair. The remaining two N lone pairs interact with the P lone pair in a π manner. Model D, which is the one suggested by Lappert and co-workers,⁴ has C_{3v} local symmetry with all three N lone pairs interacting with the P lone pair in a π fashion. It should be noted that several "intermediate" models not shown in Figure 2 were considered in this study also, such as one possessing C_3 local symmetry with the three N lone pairs skew to the P lone pair in a "propeller-like" arrangement.

For each of the models crude "lone-pair" molecular energy level diagrams were constructed such as that shown in Figure 3 for model B. The energy level diagrams account only for direct "through-space" σ interactions between N lone pairs and/or π interactions between N and P lone pairs or through-space π interactions between N lone pairs. Through-bond interactions through the pyramidal phosphorus between the N lone pairs in molecules I–III should be small because of the nonfavorable arrangement of the orbitals containing the lone pairs, and these have been neglected as they were in the two previous studies.^{2,4} For each of the energy level diagrams the first four ionization potentials from the photoelectron spectrum of I, II, or III can be equated to the negatives of the orbital energies (Koopmans' theorem), and four simultaneous equations can be written for the ionization potentials in terms of the various interaction parameters and basis orbitals. The resulting set of equations for the orbital sequence in Figure 3 is

$$I_1 = N_0 - \beta^{\sigma}_{NN} \quad (1)$$

$$I_2 = P_0 - \beta^{\pi}_{NP} \quad (2)$$

$$I_3 = N_0 + \beta^{\pi}_{NP} \quad (3)$$

$$I_4 = N_0 + \beta^{\sigma}_{NN} \quad (4)$$

where, N_0 and P_0 are the energies of the nitrogen and phosphorus basis orbitals, respectively; β^{σ}_{NN} represents the σ interaction between the two nitrogen lone pairs which are orthogonal to the phosphorus lone pair, and β^{π}_{NP} represents the π interaction between the remaining nitrogen lone pair and

Table II. Interaction Parameters for the Tris-dialkylaminophosphines^a

Compd	N_0	P_0	β^{σ}_{NN}	β^{π}_{NP}
$P[N(CH_3)_2]_3$	8.74	7.92	1.15	0.01
$P[N(CH_2CH_3)_2]_3$	8.34	7.81	1.14 ₅	0.12
$P[N(CH_2CH_2CH_3)_2]_3$	8.19	7.73	1.14	0.15

^a All values are in eV.

the phosphorus lone pair. The set of equations can be solved for values for N_0 , P_0 , β^{σ}_{NN} , and β^{π}_{NP} . This procedure was carried out for each of the models for compounds I–III. Furthermore, for each model the various possible positions of P_0 with respect to N_0 were explored. Cowley and co-workers² assumed that P_0 should be much more stable than N_0 so that

$$I_1 = N_0 - \beta^{\sigma}_{NN} \quad (5)$$

$$I_2 = N_0 - \beta^{\pi}_{NP} \quad (6)$$

$$I_3 = N_0 + \beta^{\sigma}_{NN} \quad (7)$$

$$I_4 = P_0 + \beta^{\pi}_{NP} \quad (8)$$

The only model which is completely consistent with the experimental data for compounds I–III is model B, the one proposed earlier² by Cowley and co-workers. However, our data indicated that the energy level scheme shown in Figure 3 is the correct one rather than the scheme proposed by Cowley et al.,² which assumes a very stable phosphorus basis orbital, P_0 . Our current values for the parameters N_0 , P_0 , β^{σ}_{NN} , and β^{π}_{NP} are given in Table II. One notes that the value of basis orbital N_0 is affected more by alkyl substitution than is that of P_0 . This is reasonable because the alkyl groups are directly bonded to N, not to P. The N–N σ interaction (β^{σ}_{NN}) is almost constant throughout the series and is much larger than the N–P π interaction (β^{π}_{NP}). This is reasonable because the phosphorus lone-pair orbital is larger and more diffuse than is the nitrogen lone-pair orbital which may interact with it; also, the pyramidal phosphorus lone-pair orbital is not oriented favorably for efficient overlap with the nitrogen lone pair orbital. As the nitrogens approach planarity with phosphorus, this π interaction should increase. This is completely consistent with the data in Table II because β^{π}_{NP} increases as the size of the alkyl group increases. The larger alkyl groups (propyl) should sterically interact to greater extent than the smaller ones (methyl), thus forcing the phosphorus of II and III closer to planarity and allowing more efficient π overlap than is the case for I.

None of the other models were consistent with the data for I–III. The Cowley model with its very stable P_0 gives a decrease in N_0 of 0.34 eV and in P_0 of 0.30 eV upon passing from I to II. This does not seem to be a large enough difference given the fact that the perturbing moiety (the alkyl group) is attached directly to nitrogen. Furthermore, this version of model B predicts a decrease in β^{π}_{NP} from I to III which would not seem reasonable if steric interaction forces II and III toward planarity. The Lappert model (model D) is more difficult to treat by our crude MO method because the C_{3v} symmetry introduces the necessity for Jahn–Teller splitting to account for four bands in the spectrum and leaves us with only three equations with four unknowns, e.g.

$$I_1 = P_0 - \beta^{\pi}_{NP} \quad (9)$$

$$(I_2 + I_3)/2 = N_0 - \beta^{\sigma}_{NN} \quad (10)$$

$$I_4 = N_0 + 2\beta^{\pi}_{NP} + \beta^{\sigma}_{NN} \quad (11)$$

Assigning various values to P_0 and solving for the other parameters, inconsistencies in the data for I–III were always noted; e.g., β^{π}_{NP} decreased from I to III. But the best arguments against model D have been advanced very recently

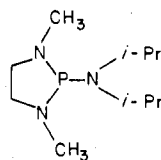
by Cowley and collaborators.⁵ We agree with those arguments. Model A, which is also a C_{3v} model, can be treated by our crude MO arguments because one of the ionization potentials can always be equated to P_0 , while the others may be fit by only two parameters, e.g.

$$I_1 = N_0 - 2\beta_{NN}^{\sigma} \quad (12)$$

$$I_2 = P_0 \quad (13)$$

$$(I_3 + I_4)/2 = N_0 + \beta_{NN}^{\sigma} \quad (14)$$

The parameters obtained for all of the combinations of N_0 and P_0 using this model were inconsistent with the data. Furthermore, Cowley and co-workers have studied recently⁵ the photoelectron spectrum of the caged compound $P[N(CH_3)CH_2]_3CCH_3$ for which model A must apply. The spectrum obtained for this compound did not even remotely resemble those for I–III, and the Jahn–Teller splitting was too small to be resolved. Model C can be treated by our MO method; again all combinations of P_0 and N_0 produced results inconsistent with the data for I–III. Recent results in these laboratories on the photoelectron spectrum of the molecule



which has been demonstrated⁹ by low-temperature ^{13}C NMR to have a structure consistent with model C, indicate that model C cannot be the correct one for I–III. It should be noted that attempts in these laboratories to freeze out II and III in the low-temperature ^{13}C NMR spectra in hopes of obtaining additional proof of their structures has not been successful to date, although considerable line broadening was observed near 130 K.

Conclusions

Our results indicate that the interpretation originally proposed by Cowley et al.² is basically correct. Namely,

tris(dialkylaminophosphines) have local C_3 symmetry with only one nitrogen lone pair interacting with the phosphorus lone pair. However, we propose that bands I_2 and I_3 refer to the phosphorus–nitrogen lone pair interaction rather than bands I_2 and I_4 as concluded by Cowley et al. or bands I_1 and I_4 as concluded by Lappert et al.⁴

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Registry No. I, 1608-26-0; II, 2283-11-6; III, 5848-64-6.

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Periodic Trends in Metal–Metal Bond Character Based on Cobalt-59 Nuclear Quadrupole Resonance Spectroscopy

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^{59}Co nuclear quadrupole resonance data in the $-Co(CO)_4$ group bound to the elements bismuth, silicon, germanium, tin, lead, gallium, indium, thallium, zinc, cadmium, mercury, gold, manganese, and cobalt are discussed. The metal–cobalt bond covalency is found to increase going vertically down the periodic chart in groups 2B, 3A, and 4A. The horizontal trend is to increase covalency from left to right; that is, M–Co covalency is group 1B < group 2B < group 3A < group 4A < group 5A. There is no strong evidence for metal–metal π bonding in the majority of the compounds. The σ -bond character overall is the dominating feature. However, an interaction of the π^* level of the equatorial CO groups in $-Co(CO)_4$ with the metal–cobalt bond or the heterometal itself appears to exist based on (1) the lack of correlation between the highest frequency symmetric CO stretching mode and the cobalt coupling constants and (2) the ^{115}In NQR data in $In[Co(CO)_4]_3$ compared to those in $In[Mn(CO)_5]_3$.

Introduction

The determination of differences in metal–metal bond characteristics for a wide range of metals requires a technique that is able to sample electron density information at the bond itself. In this paper, nuclear quadrupole resonance spectroscopy was used to examine the ^{59}Co electric field gradient

in a series of $M-Co(CO)_4$ compounds where M is varied through as wide a series of metals as possible. The electric field gradient detected in the NQR experiment is sensitive to changes in the orbital populations on the cobalt atom. Through electric field gradient changes it should be possible to qualitatively order metal–cobalt bond covalency both vertically and