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The Intensity of Ligand Absorption

Shing-Bong Chen
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THE INTENSITY OF LIGAND ABSORPTION

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Shing-Bong Chen
August 1973
THE INTENSITY OF LIGAND ABSORPTION

APPROVED July 3, 1973

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Director of Thesis

[Signature]
[Name]

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Dean of the Graduate School
I would like to express gratitude to my research advisor, Dr. Earl F. Pearson, who has given freely of his time and knowledge to show me the way to scientific research. His critical advice and encouragement are especially appreciated. In addition, I wish to thank the members of the Department of Chemistry of Western Kentucky University for their invaluable discussions and suggestions. I also wish to thank Mrs. Linda Moore for typing this thesis.

Shing-Bong Chen
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ABSTRACT

The ultraviolet absorption spectra of a number of aryl phosphines and amines and transition metal complexes of triphenylphosphine have been determined. These data indicate that the intensity of the \( \pi^* \rightarrow \pi \) phenyl ring transition is not only sensitive to the central atom attached to the ring but is also affected by the metal ion in the complex. Since the degree of covalency depends on the degree of back donation, the oxidation state of the metal ion was found to be the most important factor in determining the intensity of the absorption. The more covalent the metal-phosphine bond, the lower is the intensity of the \( \pi^* \rightarrow \pi \) transition of the phenyl ring. The increase in the \( \pi^* \rightarrow \pi \) absorption intensity can be explained in terms of a reduction of the phenyl ring symmetry from \( D_{6h} \) to \( D_{2h} \) or \( C_{2v} \).
INTRODUCTION

Few studies of bonding changes in ligands after complexation have been undertaken. The \( \pi^* \rightarrow \pi \) forbidden transition of the phenyl ring becomes allowed by vibrational perturbations and changes in \( \pi \)-orbital symmetry. This offers a convenient means of monitoring such changes in bonding involving the phenyl ring. The intensity of \( \pi^* \rightarrow \pi \) transitions is determined by the degree of lone pair electron donation to the phenyl ring from the phosphorus atom and the degree of polarization of the phenyl rings by the metal ion of the complexes.

The objective of this work was to determine what factors such as d-electron configuration, back donation, oxidation state on the metal ion, covalency, etc. influence the intensity of the \( \pi^* \rightarrow \pi \) transition in triphenylphosphine complexes. The region of wavelength covered by this research did not show charge transfer bands. These spectra have a shoulder near 270 nm which may correspond to an unknown absorption band in benzene. The same shoulder appears on all the complexes and triphenylphosphine itself and it is, therefore, unlikely that this is a charge transfer band.
I. THEORETICAL

A. Classification of Electronic States

The nuclei of polyatomic molecules are held together by the electrons. Different electronic states of molecules arise depending upon the orbitals in which the electrons are located.

The total energy of the molecule (neglecting spin and magnetic interactions) is equal to Hamilton's function:

\[ H = T + V \]  

where \( T \) is the kinetic energy of the electrons and the nuclei and \( V \) is the potential energy of the electrons and nuclei due to the electrostatic field. In wave mechanics, the total energy of a stationary state of the molecule is represented by Schrödinger's equation\(^1\)

\[ H\psi = E\psi \]  

or

\[ \frac{1}{m} \sum_i \left( \frac{\partial^2 \psi}{\partial x_i^2} + \frac{\partial^2 \psi}{\partial y_i^2} + \frac{\partial^2 \psi}{\partial z_i^2} \right) + \frac{1}{k^2 M_k} \left( \frac{\partial^2 \psi}{\partial x_k^2} + \frac{\partial^2 \psi}{\partial y_k^2} + \frac{\partial^2 \psi}{\partial z_k^2} \right) + \frac{8\pi^2}{\hbar^2} (E-V) \psi = 0 \]  

where \( x_i, y_i, \) and \( z_i \) are the coordinates of the electrons with mass \( m \) and \( x_k, y_k, \) and \( z_k \) are the coordinates of the nuclei with mass \( M_k. \) \( E \) is total energy and \( V \) is the potential energy. Since the velocity of the
electrons is much faster than that of the nuclei, the motion of the electrons can be considered in the field of fixed nuclei. In this case (Born-Oppenheimer Approximation\textsuperscript{2}), the total wave function can be written as the product of two wave functions.

\[ \psi = \psi_e (..., X_i, Y_i, Z_i, ...) \psi_n (..., X_k, Y_k, Z_k, ...) \]  

where \( \psi_e \) is the wave function describing electron motion and \( \psi_n \) is that for the nuclear motion.

The potential energy of the electrons has the symmetry of the molecule in a particular electronic state. For non-degenerate states, the eigenfunction can only be symmetric or antisymmetric with respect to the symmetry operations. For degenerate states, the eigenfunction can change into a linear combination of two or more degenerate eigenfunctions.

A symmetry operation is a movement of the coordinate system of the molecule. The position and orientation of the coordinate system is noted before and after the movement is carried out. If these two positions and orientations are indistinguishable, but not necessarily identical, the operation is a symmetry operation applicable to the molecule under consideration.

The symmetry operations can be represented by matrix multiplication. The symmetry operations which are conjugate to one another define a class of the group. So, it is possible to reduce a given matrix representation to an irreducible representation. The sum of the diagonal elements in each of the matrices in these irreducible representations is called the character of the irreducible representation.
The dimensions of the character table depend upon the number of classes, with one irreducible representation for each class.

Any eigenfunction of the Hamiltonian must belong to one of the irreducible representations (A or B for one-dimensional representations, E for two-dimensional representations and T for three-dimensional representations). Thus, symmetry can be used to classify the states of molecules and the electronic transitions between these states.

The symmetry of a molecule places restrictions upon the possible electronic transitions which can occur. While Group Theory can not be used to determine the absolute intensity of an electronic transition, Group Theory can be used to determine when the intensity must be identically zero and gives rise to selection rules. These concepts are discussed in more detail in Section B which follows.

B. Selection Rules

Electronic transitions are represented in quantum mechanics by the equations:

\[ E' - E'' = h\nu \]  \hspace{1cm} (5)

and

\[ \vec{R} = \int \psi^* \mu \psi \, d\tau \]  \hspace{1cm} (6)

where \( \vec{R} \) is the transition moment and \( |\vec{R}|^2 \) is proportional to the intensity of the absorption band. \( \mu \) is an operator for instantaneous dipole moment and may be written in terms of the three classical components of an electronic dipole

\[ \mu = \mu_x + \mu_y + \mu_z \]  \hspace{1cm} (7)
The selection rules for electronic transitions in atoms can be summarized:

\[ g \leftrightarrow u \quad g \leftrightarrow g, u \leftrightarrow u \]
\[ \Delta S = 0 \]
\[ \Delta L = 0, \pm 1 \quad L = 0, \leftrightarrow L = 0 \]
\[ \Delta J = 0, \pm 1 \quad J = 0, \leftrightarrow J = 0 \]
\[ \Delta M = 0, \pm 1 \]

The electronic states of some centrosymmetric polyatomic molecules have gerade (even) character. We would predict the transition moment, \( \vec{R} \), to be zero for transitions between such states (zero absorption intensity) because the direct product of two \( g \) functions in \( \vec{R} \) (Eq. 6) can never span any ungerade (uneven) representations. In practice, the center of symmetry of these molecules is temporarily removed by an unsymmetrical vibration. These transitions do take place when the electronic transition occurs with simultaneous excitation of one or more vibrational modes (Vibronic Coupling) but with only about \( 10^{-3} \) times the intensity of electronically allowed transitions. Vibronic perturbations are more important in polyatomic molecules than in diatomic molecules because diatomic molecules have only one vibrational mode. The eigenfunction, \( \psi \), can be written in the Born-Oppenheimer approximation as:

\[ \psi_{ev} = \psi_e \cdot \psi_v \quad (8) \]

From equations (6) and (8), we obtained:

\[ \vec{R}_{ev} = \int \psi_e^* \cdot \mu \cdot \psi_v \, d\tau_{ev} \]
\[ \vec{R}_{ev} = \int \psi_e^* \cdot \mu \cdot \psi_v \, d\tau_e \int \psi_v^\dagger \cdot \psi_v \, d\tau_v \quad (9) \]
In order for electronic transitions from the ground state to the excited state to occur, the direct product of the symmetry representations of the wave functions \( \Gamma_{\psi'_{ev}} \otimes \Gamma_{\psi''_{ev}} \) must transform, or have a component that transforms, like a translation (Electronic transitions involve movement of the electron.). In other words, the product, \( \Gamma_{\psi'_{ev}} \otimes \Gamma_{\psi''_{ev}} \), or its components, must transform as \( \Gamma_{T_x}, \Gamma_{T_y}, \) or \( \Gamma_{T_z} \); for only in this manner can the direct product, \( \Gamma_{\psi'_{ev}} \otimes \Gamma_{\psi''_{ev}} \), contain the totally symmetric group representation.

From Group Theory, the representation of the direct product, \( \Gamma_{AB} \), will contain the totally symmetric representation only if the non-degenerate irreducible representations are identical (\( \Gamma_A = \Gamma_B \)). Although the integral, \( \int \psi_{e}^{*} \mu_{e} \psi_{e} d\tau_{e} \), may be zero for the electronic transition, the integral, \( \int \psi_{e}^{*} \mu_{e} \psi_{e} d\tau_{e} \), can be non-zero if the representation of \( \psi_{e}^{*} \mu_{e} \psi_{e} \) is, or contains, the symmetry of one of the vibrations of the molecules, i.e., \( \Gamma(\psi_{e}^{*} \mu_{e} \psi_{e}) = \Gamma_{\psi'_{ev}} \). In this manner, \( \Gamma_{\psi'_{ev}} \otimes \Gamma_{\psi''_{ev}} \) contains the totally symmetric representation and the transition becomes vibronically allowed but electronically forbidden. Vibronically allowed transitions are weak (low intensity) and "borrow" intensity from a nearby allowed transition. These transitions occur in free molecules in the absence of coordination to metal ions. Other transitions in transition metal complexes that do not exist in uncomplexed molecules are discussed in Section D.
C. Transition Metal Complexes

In the first transition series of the neutral atoms, the energies of the 3d-orbitals and 4s-orbitals are very similar. As the positive charge on the transition-metal ion increases, the 3d-orbitals become more stable relative to the 4s-orbital. In complexes, the 4s-orbital is empty and electrons are in the 3d-orbitals. In the free ion, the d-orbitals \((d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{zx})\) have the same energy. However, the d-orbitals are not all equivalent in complexes. The degeneracy is split by the electrostatic field of the ligands. In an octahedral configuration, the \(t_{2g}\) energy level \((d_{xy}, d_{yz}, d_{zx})\) lies at lower energy than the \(e_g\) energy level \((d_{z^2} \text{ and } d_{x^2-y^2})\). The splitting between the \(t_{2g}\) and \(e_g\) levels is designated \(\Delta_0\) and relates to the strength of the ligand electrostatic field. In a tetrahedral configuration, the \(t_{2g}\) and \(e_g\) levels are in the inverse order, with the \(t_{2g}\) level being higher in energy than the \(e_g\) level. The energy difference between the \(t_{2g}\) and \(e_g\) orbitals is \(\Delta_t\). From the simplest electrostatic model with all the distances the same in both the octahedral and tetrahedral cases, \(\Delta_0\) and \(\Delta_t\) are related as:

\[
\Delta_t = \frac{4}{9} \Delta_0
\]

The bonding in transition metal complexes can be described in Pearson's hard-soft acid-base concept. Ligands can be divided into soft bases which are polarizable, and hard bases which are nonpolarizable. The "hardness" of the acid (metal ion) increases with decreasing size and increasing positive oxidation state. Hard acids prefer to associate with hard bases by ionic forces, and soft acids prefer soft bases in which the
interaction is more covalent in nature. Using the same ligand, the covalency of the metal-ligand bond depends on the character of the acid. Metals with low or zero oxidation state, and/or of large size, are soft acids. These are expected to form strong covalent bonds with soft bases. This is also in agreement with the Nephelauxetic Effect. The interelectronic repulsion energy is described as a function of the Racah Parameter (B). The lone pairs of electrons of the ligands can delocalize into the d-shell of the metal and expand the d-shell. This delocalization increases the mean distance between the d-electrons and enhances the covalency of metal-ligand bonds. This is expressed by the nephelauxetic ratio $\beta$ as:

\[
\beta = \frac{B \text{ in complex}}{B \text{ in free ion}}
\]

Increasing the mean distance of the d-electrons in the complexes will decrease the interelectronic repulsion, i.e. lower the value of $B$ and, thereby, reduce the ratio ($\beta$). The $\beta$-value decreases with the ligand in the Nephelauxetic series as:

\[
\text{free ion} > F^- > H_2O > CO(NH_2)_2 > NH_3 > NH_2CH_2CH_2NH_2 \\
\sim (CO_3)^{2-} > NCS^- > Cl^- > CN^- > Br^- > S^{2-} \\
\sim (C_2H_5O)_2PS_2^- > I^- > (C_2H_5O)_2PSe_2^-
\]

In terms of the donor atom, the series is:

\[
F > O > N > Cl > Br > S > I > Se
\]

Furthermore, soft acids have the potential for d- or p-electron donation into suitable ligand orbitals via $\pi$-bonds. Some neutral mole-
cules such as carbon monoxide, isocyanides and triphenylphosphine, etc., with π electron acceptor orbitals, can form complexes with transition metals. These ligands possess vacant π-orbitals in addition to lone-pairs of electrons. These vacant orbitals accept electron density from the filled metal orbitals to form a type of π-bonding that supplements the σ-bonding arising from lone-pair donation. This phenomenon has been named "back bonding" and "synergic effect." From the electrostatic viewpoint, the greater the back donation, the greater is the σ-bond formation and vice versa. This effect has been studied most in carbonyl complexes. It is believed that the CO group transfers an electron to the metal while the metal transfers an electron to a π* orbital of the CO group. If back donation from the metal increases, the metal-carbon bond becomes stronger and the carbon-oxygen bond becomes weaker. This effect is clearly shown by comparison of the infrared stretching frequency of free carbon monoxide with that of its complexes. The infrared frequency ν_{CO} of free carbon monoxide is 2155 cm^{-1} and decreases with the extent of M \rightarrow C back-bonding as indicated by the ν_{CO} frequencies for the complexes listed below:

\begin{align*}
\text{Mn(CO)}_6^+ & \quad \text{Cr(CO)}_6 \quad \text{V(CO)}_6^- \\
2096 & \quad 2000 \quad 1859 \text{ cm}^{-1} \\
\text{Ni(CO)}_4 & \quad \text{Co(CO)}_4^+ \quad \text{Fe(CO)}_4^{2-} \\
2046 & \quad 1883 \quad 1788 \text{ cm}^{-1}
\end{align*}

D. Charge Transfer Spectra (CTS)

The electron may be excited from a molecular orbital centered on the metal to one centered on the ligand, or vice versa. In general, charge transfer transitions occur in an accessible spectral region only
in complexes of easily oxidized metals with easily reduced ligands or complexes of easily reduced metals with easily oxidizable ligands. Indeed, all complexes must exhibit charge transfer spectra. In most complexes, charge transfer processes are of higher energy than the weaker d-d transitions and usually lie in the extreme blue end of the visible spectrum, or in the ultraviolet and far ultraviolet region of the electromagnetic spectrum. These intense absorptions may mask the weaker crystal field transitions.

Figure 1 shows a molecular orbital diagram for a typical complex and the five types of transition that are expected.

\[
\begin{align*}
v_1 : e_g & \leftrightarrow t_{2g} \\
v_2 : t_{2g}(\pi^*) & \leftrightarrow \pi \\
v_3 : e_g(\sigma^*) & \leftrightarrow \pi \\
v_4 : t_{2g}(\pi^*) & \leftrightarrow \sigma \\
v_5 : e_{2g}(\sigma^*) & \leftrightarrow \sigma
\end{align*}
\]

The Laporte forbidden d-d transition, \(v_1\) type, may occur if the metal ion orbitals overlap with ligand orbitals. In centrosymmetric molecules, odd molecular vibrations can couple the even d-orbital wave functions with odd excited wave functions thus mixing some odd character into the d-orbitals (see Chapter II). The d-orbitals of the metal ions are not pure metal-ion d-orbitals. In non-centrosymmetric molecules the even character of the d-orbitals is removed by overlap of the metal-ion and ligand orbitals. All the d-d transitions should be weak. The molar extinction coefficient is usually smaller than 50 \(\ell/\text{mole} \cdot \text{cm}\). In octahedral complexes, these d-d transitions usually lie between 7500 \(\text{cm}^{-1}\).
Figure 1. A Simplified Molecular Orbital Diagram for an Octahedral $\text{MX}_6$ Complex, Showing the Potential Ligand to Metal Charge-Transfer Transitions.$^{10}$
Metal

Molecular Orbital

Ligand
and 12,500 cm\(^{-1}\) for divalent ions of the first transition metal series.\(^{11}\) However, the greater the covalency of metal-ligand bond, the greater is the intensity of the crystal field transition (d-d transition). The perturbations of forbidden transition by odd vibrations in centrosymmetric molecules is discussed in more detail in Section F which follows.

There are two broad classes of charge transfer bands for complexes—Ligand-to-Metal (L \(\rightarrow\) M) and Metal-to-Ligand (M \(\rightarrow\) L) charge transfers. Ligand-to-Metal transitions of \(\nu_2\) type (see Figure 1) will be of lowest energy for the charge transfer bands and lie in the region 15,000 cm\(^{-1}\) - 30,000 cm\(^{-1}\) with relatively narrow bands because both the \(\pi\) and \(\pi^*\) orbitals are non-bonding and the M - L distance will not vary appreciably during the transition. These narrow bands are absent in high-field octahedral d\(^6\) (t\(_{2g}\)\(^6\)) complexes, since electrons cannot move from the \(\pi\)-orbital to the t\(_{2g}\) orbital if the t\(_{2g}\) level is already full. The lowest energy charge transfer bands in octahedral t\(_{2g}\)\(^6\) complexes is expected to be of \(\nu_3\) type which lie between 25,000 cm\(^{-1}\) and 45,000 cm\(^{-1}\). Since the transition is from a mainly non-bonding level to an antibonding level, the bands should be broad (2,000 - 4,000 cm\(^{-1}\)). Transitions of the \(\nu_4\) type are expected to be broad and weak. The high intensity bands of \(\nu_5\) type, in many cases, lie beyond the range of observation. Metal-to-Ligand (M \(\rightarrow\) L) type transitions are expected when the ligand has low lying orbitals, usually unsaturated ligands with empty \(\pi\) antibonding orbitals, and the metal ion has filled orbitals (readily oxidizable transition metal ion).
E. The Jahn-Teller Effect

Jahn and Teller have proved a rather remarkable theorem which states that if the electronic state of a non-linear molecule is degenerate, the molecule will distort to a lower symmetry and more stable configuration (see Figure 2). For small coupling of electronic and vibrational motions, according to perturbation theory, the magnitude of the splitting is determined by: \( ^{13} \)

\[
\int \psi_p^0 H' \psi_q^0 \, dt_e = \sum_i \int \psi_p^0 \left( \frac{\partial H_e}{\partial Q_i} \right)^0 Q_i \psi_q^0 \, dt_e
\]  

(10)

Where \( H' \) is the perturbation operator, \( Q_i \) is a normal coordinate and \( \psi_p^0 \) and \( \psi_q^0 \) are linearly independent wave functions for the doubly degenerate state. Totally symmetric vibrations do not tend to reduce the symmetry of the molecule and are not effective in splitting electronic degeneracies and making the molecule more stable. The integral is nonzero as a result of destroying the molecular symmetry, if an appropriate non-totally symmetric vibration is present. The non-totally symmetric vibrational representation must contain the representation for the doubly degenerate electronic state, if the degeneracy is to be removed by the Jahn-Teller Effect. Degenerate representations of high symmetry molecules correlate with two or more non-degenerate representations for the distorted molecule of lower symmetry.

F. The 260 nm Electronic Transition of Benzene

In the ground state of benzene, the 6 \( \pi \)-electrons are added to the lowest energy orbitals first, according to Hund's Rule and the Pauli Principle. The ground state \( ^1A_{1g} \) is formed from the configuration
Figure 2. The Effect of a Jahn-Teller Distortion upon an Octahedral Complex by Elongation along One Axis.
\((a_{2u})^2(e_{1g})^4\) (see Figure 3). Where \(\alpha\) is the energy for zero interaction of the \(p_z\) orbitals and \(\beta\) is a negative quantity relating to the resonance interaction. The lowest energy is \(\alpha + 2\beta\) \((a_{2u})\) and the highest is \(\alpha - 2\beta\) \((b_{2g})\). The lowest excited states are obtained by promoting an electron from the \(e_{1g}\) orbital to the next higher orbital of \(e_{2u}\) symmetry. The configuration \((a_{2u})^2(e_{1g})^3(e_{2u})^1\) gives rise to \(^3B_{1u},^3B_{2u},^3E_{1u},^1B_{1u},^1B_{2u},^1E_{1u}\) electronic states as illustrated in Figure 4. The energies of these states are different due to electron-electron repulsions. The first known singlet-singlet ultraviolet absorption of benzene vapor near 260 nm is assigned to the \(^1B_{2u} + ^1A_{1g}\) transition.\(^{15}\)

Goeppart-Mayer and Sklar\(^{16}\) and most recently Parr, Craig and Ross\(^{17}\) have calculated the energies of these singlet excited states by LCAO/MO methods. There is general agreement that the relative energy is in the order of \(^1B_{2u} < ^1B_{1u} < ^1E_{1u}\). This order is in agreement with experimental observations.\(^{18}\) The 260 nm \((^1B_{2u} + ^1A_{1g})\) absorption represents a transition electronically forbidden by symmetry selection rules. The electronic transition occurs due to coupling to a vibration of \(e_{2g}\) or \(b_{1g}\) type.\(^{19}\) (See Section B of Chapter I). In fact, there is no \(b_{1g}\) vibration in benzene.\(^{20}\) The direct product of \(\Gamma_{e'} \otimes \Gamma_{u} \otimes \Gamma_{e''}\) should be equal to or contain \(\Gamma_{v'}\). The symmetry of the perturbing vibration is given by:

\[ B_{2u} \otimes E_{1u} = E_{2g} \]

(See Table 1) where \(e_{2g}\) is the representation of the \(v_{18}\) vibration\(^*\)

(See Figure 5).\(^*\)\(^{v_{16}}\) and \(v_{18}\) are the most active of the four \(e_{2g}\) type vibrations in this \(^1B_{2u} + ^1A_{1g}\) electronic transition in benzene.\(^{22}\) Craig's calculations\(^{23}\) for the electronic transition show the \(v_{18}\) vibrational mode to be more intense than \(v_{16}\) in the ratio of 230:1.
Figure 3. \(\pi\)-Electron Energy Levels in Benzene from the Hückel Approximation
\[ \begin{align*}
\text{b}_{2g} & \quad \alpha - 2\beta \\
\text{e}_{2u} & \quad \alpha - \beta \\
\alpha & \\
\text{e}_{1g} & \quad \alpha + \beta \\
\text{a}_{2u} & \quad \alpha + 2\beta
\end{align*} \]

Ground State  Excited State
Figure 4. Observed Low Excited States of Benzene*14

*The prediction of the two states $^3E_{1u}$ and $^3B_{2u}$ which have not been observed are indicated by broken lines.
\begin{align*}
\begin{array}{c}
E(\text{eV}) \\
7.0 \\
6.0 \\
5.0 \\
4.0 \\
3.0 \\
2.0 \\
1.0 \\
0.0
\end{array}
\end{align*}
\begin{align*}
\left\{ \begin{array}{c}
1_{E_{1u}} \\
1_{B_{1u}} \\
3_{B_{2u}} \\
1_{B_{2u}} \\
3_{E_{1u}} \\
3_{B_{1u}} \\
1_{A_{1g}} \\
(a_{2u})^2(e_{1g})^4 \end{array} \right. & \Rightarrow \quad (a_{2u})^2(e_{1g})^2(e_{2u})^1
\end{align*}
## TABLE 1

**D\textsubscript{6h} POINT GROUP CHARACTER TABLE\textsuperscript{21}**

<table>
<thead>
<tr>
<th>( \text{D}_{6h} )</th>
<th>E</th>
<th>2\text{C}\textsubscript{6}</th>
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Figure 5. The $e_{2g}$ Type Normal Vibrations of the Benzene Molecule$^{24}$

(point group $D_{6h}$)
The intensity in the 260 nm transition in benzene vapor is a measurement of the ring distortion due primarily to the $v_{18}$ vibrational mode. In triphenylphosphine and other benzene derivatives, the intensity is due to other factors which are discussed in more detail in Chapter III which follows.
II. EXPERIMENTAL

A. Preparation of Complexes

All metal chlorides and triphenylphosphine were reagent grade and were used without further purification. All complexes were previously known and literature preparations were repeated with little modification. All the physical properties of the compounds obtained in the synthesis matched those listed in the literature reference cited.

1. Bis(triphenylphosphine) Complex of Iron(III) Chloride

The compound was precipitated from triphenylphosphine (6 g) and anhydrous iron(III) chloride (1.62 g), both dissolved in ethylacetate. The complex was scraped from the walls, washed with anhydrous ethyl ether and dried. Black crystals with green reflections were obtained which had the following properties: m.p. 114°C; soluble in ethyl acetate, methanol acetonitrile; unstable in humid air or alcohol; insoluble in diethyl ether or benzene.

2. Dichlorobis(triphenylphosphine)iron(II)

Iron(II) chloride tetrahydrate (2.0 g) in benzene was refluxed with a Dean-Stark trap for 1 hour, dehydration being accompanied by a change from pale green to white. Triphenylphosphine (10.5 g) was added and the mixture boiled in benzene (60 ml) for 6 hours under dry nitrogen. The mixture was filtered while hot, filled with N₂ gas and stored overnight. The almost colorless crystals, formed from the brown solution, were filtered and
washed with benzene. The compound is unstable in solution, particularly in hydroxylic solvents. However, under nitrogen gas, the solid is stable indefinitely, m.p. 165°C.

3. Dichlorobis(triphenylphosphine)cobalt(II)*
Powdered cobalt(II) chloride hexahydrate (2.39 g) was added to melted triphenylphosphine (7.86 g). The blue product was treated with hot ethanol and filtered. The compound was further washed with hot ethanol to yield 5.5 g of product, m.p. 230°C.

4. Chlorotris(triphenylphosphine)copper(I)
Copper(I) chloride (1 g) was added to melted triphenylphosphine (11.8 g). The white paste obtained was dissolved in chloroform and filtered. The solution was then treated with n-heptane to yield 5.0 g of product, m.p. 167°C.

5. Dichlorobis(triphenylphosphine)nickel(II)
Nickel(II) chloride hexahydrate (2.4 g) was added to melted triphenylphosphine (7.8 g). The deep olive-green product formed immediately. The excess ligand was removed with hot acetic acid to yield 2.6 g of product. The compound was recrystallized from 1-butanol. The dark green crystal dissolved in acetonitrile to form a blue solution, m.p. 244°C.

---

*The Ni(II), Co(II) and Cu(I) complexes were prepared by reaction of the metal chlorides with the melted ligand. An excess of the ligand (1.5 times the stoichiometric amount) is melted in an oil bath. The temperature is kept 5°C above the melting point of the ligand while the metal salt is added slowly and for 5-10 minutes thereafter. A suitable solvent was added to wash away the excess ligand. The advantage of this method is that anhydrous metal salts are not necessary, thus eliminating one step in the preparation.
6. Chlorotris(triphenylphosphine)cobalt(I)\textsuperscript{29, 30}

A solution of cobalt(II) chloride hexahydrate (0.5 g) and triphenylphosphine (1.65 g) in ethanol (70 ml) was treated with 0.5 g of zinc at room temperature under vigorous stirring for one hour. The solution changed from a blue to green color. The resulting green precipitate was treated with 2.5 N hydrochloric acid to dissolve excess zinc, washed with ethanol and dried, m.p. 115°C.

B. Spectra

Methanol was used as the solvent for the Fe(\(\phi_3P\))\(_2\)Cl\(_2\) complex due to decomposition of this complex in other solvents. Acetonitrile was used for all other complexes. Both solvents were spectroquality and transparent above 210 nm.

The UV spectra were recorded on a Cary-14 spectrophotometer. A pair of matched 1 mm Hellma cells were used for the absorption measurements. Base lines were obtained by running pure solvent in the sample cell against pure solvent in the reference cell. The extinction coefficient (\(\varepsilon\)) has units of L/mole \cdot cm.

The spectra are shown in Figures 6-14 which follow.
Figure 6. Ultraviolet Absorption Spectra of: (A) Triphenylphosphine, (B) Triphenylphosphine Oxide.
Figure 7. Ultraviolet Absorption Spectra of: (A) Triphenylphosphine, (B) Triphenylamine.
Figure 8. Ultraviolet Absorption Spectrum of Tribenzylamine.*

*(A) Observed Spectrum, (B) and (C) Resolution of The Spectrum into its Component.
Figure 9. Ultraviolet Absorption Spectrum of Bis(triphenylphosphine) Complex of Iron(III) Chloride
Figure 10. Ultraviolet Absorption Spectrum of Dichlorobis(triphenyl-phosphine)iron(II)*

*(A) Observed Spectrum of freshly prepared complex,
(B) Spectrum after complex exposure to air for 24 hours.
Figure 11. Ultraviolet Absorption Spectrum of Dichlorobis(triphenylphosphine)cobalt(II)
Figure 12. Ultraviolet Absorption Spectrum of Dichlorobis(triphenylphosphine)nickel(II)
Figure 13. Ultraviolet Absorption Spectrum of Chlorotris(triphenylphosphine)cobalt(I)
Figure 14. Ultraviolet Absorption Spectrum of Chlorotris(triphenylphosphine)copper(I)
III. DISCUSSION

A. The Effect of Conjugation on the Intensity of the
\( \pi^* + \pi \) Transition in Benzene Derivatives.

Previous work indicates that the \( \pi^* + \pi \) \((^1B_{2u} + ^1A_{1g})\) transition, forbidden by Laporte Selection Rules, becomes allowed due to mixing of the electronic and vibrational motions of the molecule (see Section F of Chapter I). The transition becomes allowed because the \( \pi \)-electron symmetry is reduced from \( D_{6h} \) to a lower symmetry due to excitation of a non-totally symmetric vibration. The mechanism of this interaction is discussed in more detail below.

The spectral transitions of substituted benzene molecules arise by a similar effect. However, the \( \pi^* + \pi \) phenyl ring transition is allowed in the absence of coupling between the electronic and vibrational motions, since the symmetry of the molecule as a whole is less than \( D_{6h} \) in substituted benzene molecules. The effect is small, however, if the substituent cannot interact effectively with the \( \pi \)-electron system, since it is the symmetry of this system which must be reduced below \( D_{6h} \), if the transition is to be allowed. For example, toluene (and other monoalkyl benzene derivatives) shows only weak absorption in the 260 nm region. In order to cause the \( \pi^* + \pi \) transition to be strongly absorbing, the atom attached to the phenyl ring must have nonbonding electrons or empty orbitals. That is, the group attached to the ring must be a \( \pi \)-electron donor or a \( \pi \)-electron acceptor. In triphenylphosphine, the lone-pair
electrons of the phosphorus atom will delocalize with the phenyl rings to some degree. This changes the point group from the $D_{6h}$ $\pi$-electron symmetry of free benzene and leads to resonance structures of $\pi$-electron symmetry $D_{2h}$ and $C_{2v}$.

Simultaneously, the $\pi$-electron symmetry is reduced and the forbidden $^1B_{2u} + ^1A_{1g}$ transition in $D_{6h}$ symmetry becomes $^1B_{3u} + ^1A_{g}$ in $D_{2h}$ or $^1B_1 + ^1A_1$ in $C_{2v}$, both of which are allowed (see Table 2 and 3).

Hoffmann has discussed the valence orbitals of cyclopropane and cyclobutane by using Walsh's orbital treatment. His treatment indicates an interaction between orbitals which are normally considered isolated. These orbitals have higher energy than ethylene $\pi$-orbitals when a $\pi$-electron acceptor is substituted on the ring. These $\pi$-electron acceptors weaken the bonding in bonding regions and strengthen the bonding in antibonding regions. When a $\pi$ donor is substituted on the ring, the bonding is strengthened in bonding regions and weakened in antibonding regions. Both $\pi$-electron donors and $\pi$-electron acceptors reduce the symmetry of the cyclopropane or cyclobutane ring. This reduced symmetry should influence the spectra of these molecules; however, the absorption is in the far ultraviolet spectral region and is not readily accessible for study.
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<tr>
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TABLE 3

THE CORRELATION TABLE FOR THE SPECIES OF $D_{6h}$
AND ITS SUBGROUPS ($D_{2h}$ AND $C_{2v})^{32}$

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<th>$C_{2v}$</th>
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<td>$A_{1g}$</td>
<td>$A_1$</td>
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<td>$A_{2g}$</td>
<td>$B_1$</td>
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<td>$B_{2g}$</td>
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<td>$A_{2g}$</td>
<td>$A_2 + B_2$</td>
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<td>$A_{1g}$</td>
<td>$A_1 + B_1$</td>
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<td>$A_{1u}$</td>
<td>$A_2$</td>
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<td></td>
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<tr>
<td>$B_{3u}$</td>
<td>$B_{2u}$</td>
<td>$B_1$</td>
<td></td>
</tr>
<tr>
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<td>$A_1 + B_1$</td>
<td></td>
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<td>$A_u + B_{1u}$</td>
<td>$E_{2u}$</td>
<td>$A_2 + B_2$</td>
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Hoffmann also pointed out the interaction of the orbitals of the 7-norbornenyl cation.

The empty 2p-orbital of C\textsubscript{7} interacts with the π and π* orbitals of the double bond between C\textsubscript{2} and C\textsubscript{3}. The occupied π-orbital is stabilized by the through-space interaction between C\textsubscript{7} and the 2p-orbitals of C\textsubscript{2} and C\textsubscript{3}. The π*-orbital will remain unchanged. At the same time, the energy of the 2p-orbital at C\textsubscript{7} is raised by this interaction. The two π-electrons of C\textsubscript{2} and C\textsubscript{3} are delocalized over three centers (C\textsubscript{2}, C\textsubscript{3}, and C\textsubscript{7}), thus making the cation more stable overall.

In compounds like ethylenediamine,

the two lone-pairs are too far apart for the through-space interaction to be important. Thus, any interaction between the nitrogen atoms must be due to some other interaction which is called through-bond coupling. The bonding orbital between C\textsubscript{1} and C\textsubscript{2} is overlapped with the nitrogen lone-pair orbitals of like symmetry.
This interaction raises the energy of the 2p-orbitals of the nitrogen atoms and lowers the energy of the σ-orbital between C\textsubscript{1} and C\textsubscript{2}. A similar interaction between the nitrogen lone-pair orbitals and the σ*-orbital between C\textsubscript{1} and C\textsubscript{2} is also possible.

In this case, the energy of the 2p-orbitals of the nitrogen atoms is lowered and the energy of the σ*-orbital between C\textsubscript{1} and C\textsubscript{2} is raised.

Hoffmann's treatment when expanded to the benzene molecule, helps to explain the change in intensity of the π* + π transitions in benzene derivatives. Indeed, this research confirms the predictions of Hoffmann's theory. The study of the perturbation of the intensity of the π* + π phenyl ring transition offers a convenient means of detecting small changes in the symmetry of the π-electron system caused by substitution on the ring. The Walsh orbitals for the π system of benzene are of \textit{a}_2\textsubscript{u}, \textit{e}_1\textsubscript{g}, \textit{e}_2\textsubscript{u}, and \textit{b}_2\textsubscript{g} symmetry as shown in Figure 15. When electron acceptors, for example, a metal ion, remove electron density from the ring, only the occupied orbitals are affected. Because of the symmetry of the \textit{a}_2\textsubscript{u} orbital, all bonds are weakened equally. The ring expands, but the point group remains D\textsubscript{6h}. Removing electron density from the \textit{e}_1\textsubscript{g}(1) orbital
Figure 15. Molecular Orbitals of the Benzene Molecule

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[^35]
weakens the bonds adjacent to the substituent, strengthens the next bonds and weakens the two opposite bonds.

In the other component, e_{1g}(2), of the degenerate orbital the bonds parallel to the substituent are weakened when electron density is removed from the ring.

Electron donors have little effect on the filled orbitals (a_{2u}, e_g).

Adding electron density to the e_{2u}(1) orbital weakens the bonds adjacent and opposite to the substituent.

Adding electron density to the other component, e_{2u}(2), weakens the bonds parallel to the substituent.
The effect of both electron donors and acceptors substituted on the phenyl ring is to reduce the symmetry of the \( \pi \)-electron system from \( D_{6h} \) locally to \( D_{2h} \). It was shown in Chapter I that this makes the \( \pi^* \rightarrow \pi \) transition allowed and should result in an increase in the intensity of the transition. Substituted phosphorus can act as an electron donor or acceptor. This research indicates that the primary effect is electron donation from the lone-pair of electrons.

The molar extinction coefficient per phenyl ring (\( \varepsilon/\phi \)) increases from 200 \( \ell/\text{mole} \cdot \text{cm} \) for nonsubstituted alkylbenzene derivatives to 3500 \( \ell/\text{mole} \cdot \text{cm} \) for \( \Phi_3P \) (see Table 4). The vibrational features of the spectra (which is a finger print for an unperturbed benzene ring) disappear and the absorption becomes smooth (see Figure 6). The completely different spectral characteristics of triphenylphosphine indicates the entire \( \pi \)-electron system is changed. If the orbitals of the substituent were completely independent of the \( \pi \)-orbitals of the phenyl ring, the intensity of the phenyl ring absorption would not change.

Table 4 lists the molar extinction coefficient at the absorption maximum of some aryl amines, phosphines and phosphine oxides. The spectra of triphenylphosphine \([\Phi_3P]\) and triphenylamine \([\Phi_3N]\) are shown in Figure 7. Delocalization of the unshared pair of electrons into the phenyl rings implies extensive conjugation with the phenyl radical and leads to spectra in sharp contrast to free benzene or its monoalkyl
TABLE 4

THE EXTINCTION COEFFICIENT OF ARYLAMINES,
PHOSPHINES, AND PHOSPHINE OXIDES

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<th>Compound</th>
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<th>$\epsilon/\phi$</th>
<th>Reference</th>
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<td>1.17</td>
<td>5850</td>
<td>36</td>
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<tr>
<td>$\phi N(CH_3)_2$</td>
<td>0.171</td>
<td>1710</td>
<td>36</td>
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<tr>
<td>$(\phi CH_2)_3N$</td>
<td>0.457*</td>
<td>1520</td>
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<td>1.05</td>
<td>3500</td>
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<tr>
<td>$(\phi CH_2)_3P$</td>
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<td>960</td>
<td>37</td>
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<tr>
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<tr>
<td>$(\phi CH_2)_3PO$</td>
<td>0.06</td>
<td>200</td>
<td>37</td>
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*Strongly overlapped with a higher energy allowed transition. The intensity was corrected for that contributed by the other transition.
derivatives. Triphenylamine absorbs at a longer wavelength and has a higher intensity. It has been suggested that the first row elements have a greater tendency for double bond formation.\textsuperscript{36} The shift to longer wavelength, as the intensity of the transition increases, is easily comprehended if conjugation with the \( \pi \)-system occurs. The shift can be explained simply in terms of a particle constrained to a box. The spacing of the energy levels for such a system is inversely related to the size of the box. If the phenyl rings are linked by conjugation, the effective area available to the electrons increases. The spacing of the energy levels is correspondingly reduced and the absorption moves to longer wavelength (lower energy).

In triphenylphosphine oxide \([\Phi_3PO]\) and diphenylphosphinic acid \([\Phi_2PO\cdot H]\),\textsuperscript{37} the phosphorus atom does not have lone-pair electrons and can only perturb the \( \pi \)-electron system of the phenyl ring to a small degree. Two structures for \( \Phi_3PO \) can be drawn:

\begin{align*}
\text{(1)} & \quad \text{O} \\
\quad \quad \Phi \quad \Phi \quad \Phi \\
\text{(2)} & \quad \Phi \quad \Phi \quad \Phi
\end{align*}

If one of the d-orbitals of phosphorus is held in position due to bonding with oxygen (structure 1), none of the other d-orbitals can point in the proper direction or have the required symmetry to overlap with the phenyl ring. Thus, the conjugation of all the rings will be weak, the intensity of the absorption low, and the vibrational structure will appear on the absorption band. (See Figure 6.)
Tribenzylamine [(CH₂)₃N] (see Figure 8) and tribenzylphosphine [(CH₂)₃P] have features due to vibrational transitions on the 260 nm band indicating "free" benzene character. The extinction coefficients are lower than CH₂N and CH₃P respectively, because the lone-pair of electrons of the central atom (N or P) cannot easily delocalize into the phenyl ring through the methylene group.

Comparison of the spectra of triphenylamine, N-methyldiphenylamine and dimethylaniline reveals that the extinction coefficient per phenyl ring is in the order of CH₂N > CH₂NCH₃ > N(CH₃)₂. The high intensity of CH₂N can be attributed to electron delocalization throughout the entire molecule through the central N atom, as shown below:

Nitrogen and carbon are closer to the same size than phosphorus and carbon; therefore, overlap of the nitrogen orbitals with the phenyl ring is more complete. The intensity in the absorption spectra of aryl amines is, therefore, higher than that of the corresponding phosphines.

Even though the spectrum at 260 nm in tribenzylamine is strongly overlapped, it is clear that the contribution from the π* + π transition in tribenzylamine is more intense than the same transition in tribenzylphosphine. This indicates that the interaction between the phenyl ring
and the nitrogen or phosphorus atoms is transmitted quite efficiently through the bonds as indicated in Hoffmann's work.

It is attractive to draw a structure involving the d-orbitals of phosphorus and the phenyl ring to explain the increased intensity for the aryl phosphines compared to monoalkyl benzene derivatives.

This structure gives a bonding similar to the synergic bonding known to exist between the metal and phosphorus in phosphine complexes.\(^\text{39}\) This type of bonding is an important consideration in the spectra of the complexes of triphenylphosphine, as is discussed below. However, the tribenzylphosphine spectrum shows that such bonding must be of minor importance. The d-orbitals of nitrogen are too high in energy to be involved in bonding in the amines. However, the extinction coefficient per phenyl ring is higher in tribenzylamine than in tribenzylphosphine. Thus, the major influence on the spectrum is the inductive effect transmitted through the bonds of the methylene group. It is, therefore, unnecessary to postulate a direct (and improbable) overlap of the d-orbitals and the phenyl ring over or around the methylene group. Even in triphenylphosphine, the synergic bonding involving the d-orbitals on the phosphorus atom may play a minor role to the overlap of the p-orbitals with the phenyl ring since the intensity of the triphenylamine spectrum is much greater than that of the triphenylphosphine spectrum.
B. The 260 nm Absorption of Triphenylphosphine Complexes of Transition Metal Ions

Triphenylamine is an extremely weak electron donor and is not an electron acceptor. However, triphenylphosphine (P₃) is one of the most important π-acceptors. As the lone-pair electrons are donated to form a σ-bond, triphenylphosphine forms a π-bond with the metal by overlap of the filled d-orbitals of the metal with low energy, empty, antibonding orbitals (3d) of the phosphorus atom. Because of its π-acceptor character, triphenylphosphine can stabilize the lower valence states of the transition metals, forming complexes such as Ni(P₃)₄, Ni(P₃)₂Cl, etc. Table 5 lists the molar extinction coefficient (ε) near 260 nm per phenyl ring of some triphenylphosphine complexes (see Figure 9 - Figure 14). Some of the factors which influence the intensity of the absorption are discussed below.

The syngnet effect (back-donation) affects the covalency of metal-phosphine (M-P) bond. The greater the back-donation the more covalent is the M-P bond and the less the donation of the lone-pair electrons of the phosphorus atom into the phenyl rings. Reduction of the delocalization of the electrons into the phenyl rings through the phosphorus atom by conjugation causes a decrease in the intensity of the absorption. Back-donation is increased regularly with decreasing metal oxidation state. This explains the fact that the extinction coefficients of Co(P₃)₃Cl and Cu(P₃)₃Cl are lower than the free ligand P₃, and that the extinction coefficient of Co(P₃)₃Cl is lower than that of Ni(P₃)₂Cl with the same d-electron configuration.

The charge of the metal ion is an important factor (see Table 5). It can be seen that the extinction coefficient per phenyl ring of
**TABLE 5**

THE EXTINCTION COEFFICIENT OF LIGANDS IN COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon \times 10^{-4}$</th>
<th>$\varepsilon / \phi$</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe($\phi_3P$)$_2$Cl$_3$</td>
<td>2.24$^a$</td>
<td>3730</td>
<td>$O_h$</td>
</tr>
<tr>
<td>Fe($\phi_3P$)$_2$Cl$_2$</td>
<td>2.14</td>
<td>3570</td>
<td>$T_d$</td>
</tr>
<tr>
<td>Co($\phi_3P$)$_2$Cl$_2$</td>
<td>2.10</td>
<td>3500</td>
<td>$T_d$</td>
</tr>
<tr>
<td>Ni($\phi_3P$)$_2$Cl$_2$</td>
<td>2.22</td>
<td>3700</td>
<td>$T_d$</td>
</tr>
<tr>
<td>Co($\phi_3P$)$_3$Cl</td>
<td>2.88</td>
<td>3200</td>
<td>$T_d$</td>
</tr>
<tr>
<td>Cu($\phi_3P$)$_3$Cl</td>
<td>2.80</td>
<td>3110</td>
<td>$T_d$</td>
</tr>
<tr>
<td>Ni$^{2+}$N[CH$_2$CH$_2$P$_2$]$_3$</td>
<td>3.30$^b$</td>
<td>5500</td>
<td>$C_{3v}$</td>
</tr>
<tr>
<td>Ni$^{2+}$EtN[CH$_2$CH$_2$P$_2$]$_2$</td>
<td>2.50$^b$</td>
<td>6250</td>
<td>$O_h$</td>
</tr>
<tr>
<td>Ni$^{1+}$N[CH$_2$CH$_2$P$_2$]$_3$</td>
<td>1.580$^b$</td>
<td>2630</td>
<td>$C_{3v}$</td>
</tr>
</tbody>
</table>

$^a$The peak at 260 nm is actually overlapped by two other neighboring peaks.

$^b$See Reference 40.
Ni$_{2+}$N[CH$_2$CH$_2$P$_2$]$_3$ is higher than that of Ni$^{1+}$N[CH$_2$CH$_2$P$_2$]$_3$. In triphenylphosphine complexes when the charge increases, the number of chloride ions increases also. Because chloride ion has a higher $\beta$ (Nephelauxetic ratio) value than $\phi_3$P, a decrease in the covalency of M-P bond is expected. This causes an increase in the intensity of absorption. At the same time, if the charge increases, polarization of the rings is increased and the symmetry is reduced to D$_{2h}$ and the intensity increases. Polarization of the ring is confirmed by a splitting of the aromatic hydrogen resonances in the NMR spectrum of the Cu(I) complex. In addition, crystal field stabilization energies are in the order of Co$^{2+}$ ($d^7$) > Ni$^{2+}$ ($d^8$) > Fe$^{2+}$($d^6$) for tetrahedral complexes. According to this series, the covalency of M-P bond will be in the order of Co-P > Ni-P > Fe-P. If these factors are important, the extinction coefficient per phenyl ring, $\epsilon/\phi$, of the divalent ion complexes are expected to be in the order Fe$^{2+}$ > Ni$^{2+}$ > Co$^{2+}$. Experimentally, the Fe$^{+2}$ complex is not stable in solution. The partial dissociation of the complex causes a lower $\epsilon/\phi$ than Ni($\phi_3$P)$_2$Cl$_2$ (see Figure 10). Attempts were made to prepare the Ni($\phi_3$P)$_4$ complex by the method described by G. Wilke, and to prepare Ni($\phi_3$P)$_3$Cl by reaction of the Ni(II) and Ni(0) complexes. However, because both complexes are air and water sensitive, all attempts failed due to leaks in the dry box. The only trivalent complex which could be prepared was Fe$^{3+}$ and it was not stable in solution. With a suitable dry box, this work should be extended to other complexes. At least three complexes for each charge and d-electron configuration should be included. The ligand should also be changed to a multidentate type in order to assure that the ligand will not be removed in solution and that the geometry of the complex does not change. The bonding in the free ligand should be examined in more detail to see how far the influence of the
lone-pair of electrons on the phosphorus (or nitrogen) extends. If there is direct overlap of the d-orbitals with the ring through space, there may be some number of methylene groups which will again bring the phosphorus atom and the phenyl rings into proximity and cause an increase in the extinction coefficient.

C. Summary

This research has shown the \( \pi^* \rightarrow \pi \) phenyl ring transition near 260 nm to be a sensitive monitor of bonding involving phenyl rings. In every case, an increase in intensity of the transition can be explained in terms of a reduction of the local \( \pi \)-electron symmetry from \( D_{6h} \). In the case of transition metal complexes of triphenylphosphine, the change in intensity is the result of many competing factors. Therefore, no perfect correlation between the intensity of the transition and any single factor exists. However, a general trend toward higher intensity with increasing charge of the metal ion was observed and can be explained by polarization of the rings due to the inductive effect. A reduction of the intensity was also observed with increasing d-electron configuration due to metal-phosphorus back-bonding.
LIST OF REFERENCES


2. See Reference 1, p. 8.


8. See Reference 7, pp. 211, 212.


10. See Reference 7, p. 226.


15. See Reference 1, p. 178.


19. See Reference 1, p. 178.


31. See Reference 4, Appendix II, pp. 4, 6.


35. See Reference 4, p. 127.


