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ELECTRONIC TRANSITIONS OF ARYL PHOSPHINES

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Summary

Absorption and emission properties of Ph_3P, $MePh_2P$ and $Ph_2P(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$) (Ph ≡ phenyl; Me ≡ methyl) are reported. The maximum absorption band at 250 - 260 nm has been assigned to a $\pi \rightarrow \pi^*$ transition centered on the benzene ring. The lowest energy excited electronic state of the aryl phosphines has been assigned to an $1 \rightarrow a_\pi$ transition associated with an obscured absorption band at about 300 nm. The lowest excited singlet and triplet state energies are calculated to be 79 - 82 kcal mol^{-1} and 75 - 77 kcal mol^{-1} respectively.

1. Introduction

The interpretation of the absorption spectra of the aromatic phosphines such as Ph_3P (Ph ≡ phenyl) has centered around the possibility of conjugation between the non-bonding electrons of the phosphorus atom and the adjacent phenyl π system. The attachment of phosphorus to the benzene ring leads to a large increase in the absorption intensity in the region of 250 - 260 nm, which has been stated to exceed the usual increase in intensity associated with the perturbation of the symmetry of the benzene ring [1 - 4]. The various interpretations of the electronic transitions of the aromatic phosphines have associated the 250 - 260 nm absorption region to an electron excitation from the non-bonding electrons of the phosphorus into the antibonding phenyl π system [1 - 7]. Despite the extensive absorption and emission data that have been reported to date [1 - 15], the nature of the observed electronic transitions is still not clear. One of the problems is that the experimental observations reported are not consistent. For example, totally different emission spectra are reported for Ph_3P [8 - 12].

The inconsistency in the interpretation of the electronic states of the aromatic phosphines has been projected into the interpretation of the

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photoexcited state properties of the aryl phosphine copper(I) complexes [9, 13 - 15]. The results of our study on the ability of aryl phosphine copper(I) complexes to photosensitize the isomerization of norbornadiene to quadricyclane [16] suggested that a more detailed investigation of the photophysical properties of the aryl phosphines and the copper(I) complexes was needed. The investigation of the aryl phosphines reported here has led to a consistent and reasonable interpretation of the electronic transitions.

2. Experimental details

2.1. *Materials*

The aryl phosphines Ph_3P, $MePh_2P$ (Me ≡ methyl) and $Ph_2P(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$) as well as $Ph_3P{=}O$ and $MePh_2P{=}O$ were purchased commercially and used without further purification. Commercial spectroscopic benzene and cyclohexane were used. Ether–isopentane–alcohol (EPA), used as the solvent to form a rigid glass at 77 K, consists of an ethyl ether, isopentane and ethyl alcohol mixture in the volume ratio of 5:5:2 respectively. It was a commercial preparation specially purified to form a rigid glass at liquid nitrogen temperature (77 K) and to produce no appreciable phosphorescence.

2.2. *Absorption spectra*

UV absorption spectra were recorded on a Beckman Acta V UV–visible spectrometer. The phosphines were weighed in nitrogen-filled volumetric flasks and the appropriate solvent was added. The solutions were used immediately.

2.3. *Emission spectra and lifetime measurements*

A spectrophosphorimeter was designed and built from instrument components. The excitation lamp was a 300 W xenon arc lamp housed in an Oriel model C-60-53 lamp housing unit equipped with a focusing lens. The excitation monochromator equipped with variable slits was a Bausch and Lomb model 33-86-01 having a UV grating with a range of 200 - 400 nm. The rotating shutter was an Aminco–Keirs phosphoroscope accessory for the Aminco–Bowman spectrophotofluorometer. A quartz Dewar used to hold the sample had an unsilvered narrow square tip which permits passage of excitation and emission light. A 4 mm × 4 mm quartz sample tube was suspended in the Dewar by means of a finger clamp attached to the top of the Dewar. The analyzing monochromator was a Spex 1870 with a 0.5 m Czerny–Turner mounting using a Bausch and Lomb grating of 12 000 grooves per millimeter. The Spex 1870 has variable entrance and exit slits. The wavelength drive was accomplished using a Bodine motor with a variable-speed controller and brake. The monochromator was scanned at constant speeds between 25 and 50 nm min^{-1} during the recording of a fluorescence or phosphorescence spectrum. The photomultiplier tube, a

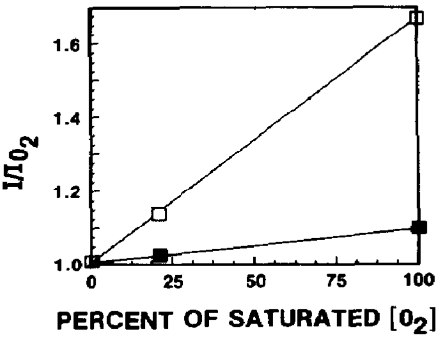
Hamamatsu R106 having a spectral response range from 160 to 650 nm, was mounted in a special Spex housing unit that attached to the exit slit of the Spex 1870 monochromator. The spectra reported are uncorrected for variations in the source and for photomultiplier response. The photomultiplier output was amplified by a Spex DPC-2 digital photometer that also contains a built-in high voltage photomultiplier power supply. Mercury emission lines (404.6, 435.8 and 546.1 nm) were used to check the accuracy of the analyzing monochromator and the scanning arrangement. The emission lines never varied more than 1 nm from the accepted values through several scans. The emission spectra of samples were recorded with and without the phosphoroscope so that both fluorescence and phosphorescence could be identified. In order to record phosphorescence spectra, the phosphoroscope speed was set high enough that no loss of intensity was observed during a complete emission cycle of the phosphoroscope. For phosphorescence lifetimes, a Tektronix 564 storage oscilloscope with a type 2B67 time base was connected directly to the photomultiplier output. The phosphoroscope speed was gradually slowed until a baseline decay could be observed during the emission cycle of the phosphoroscope. The exponential decay of the emission was then stored on the oscilloscope and a picture was taken with a Polaroid camera. Phosphorescence decay times τ_{ph} greater than about 1 ms could be measured effectively with the use of the phosphoroscope. The emission spectra and phosphorescence lifetimes of benzophenone and diphenylamine were recorded as described. The agreement with the spectra and phosphorescence lifetimes reported in the literature was within 2% [17 - 20]. The loss of intensity with the use of the phosphoroscope was calibrated by observing the phosphorescence of benzophenone with and without the phosphoroscope. The strongly overlapping fluorescent emission of the aryl phosphines was calculated by subtraction of the adjusted phosphorescent emission observed with the phosphoroscope from the total emission spectra observed without the phosphoroscope. No difference in the shape of the emission spectra was observed for a few samples in which oxygen was removed by freeze–thaw techniques.

The emission of the aryl phosphines in benzene at room temperature was extremely weak and the light scatter from the solvent had to be subtracted to obtain an accurate spectrum. A much better analysis was done by a modification of the spectrometer to allow direct input of the data into a computer. A Princeton Applied Research lock-in-amplifier model JB-5 was used in conjunction with a PAR model 125 variable-speed chopper. The output of the lock-in amplifier was compatible with an analog-to-digital (A/D) converter interface of the Apple II graphics computer. Standard 10 mm fluorescence cuvettes with a long narrow neck which could be sealed with a serum rubber stopper were used to contain the sample. The A/D converter had a built-in timer so the input to the computer could be taken at desired time intervals. The data from a scan were stored on a disk as wavelength-dependent light intensities. The background spectrum of benzene taken under the same conditions was also stored on a disk. The background spectrum was then subtracted from the sample spectrum to obtain the corrected spectrum. The corrected spectrum was numerically integrated summing small rectangular areas taken over the spectrum. The integrated areas of the fluorescent emission of the aryl phosphines were divided by the integrated fluorescent emission area of $MePh_2P$ to obtain the relative quantum yields reported. Only minor corrections were made to account for differences in absorbance since all solutions were made to show the same absorbance readings at the excitation wavelength of 313 nm. The concentrations of the aryl phosphines were about 1×10^{-3} M. Oxygen was removed by bubbling with helium. The cell was flushed with helium which had passed over hot copper turnings (650 - 700 °C) and had then been bubbled through benzene to form a saturated atmosphere to avoid solvent loss during bubbling.

The fluorescence lifetimes reported were estimated by the effect of oxygen quenching on the fluorescent emission. The fluorescent emission and integrated areas were recorded for the respective aryl phosphine with three different oxygen concentrations present in the benzene solutions. The oxygen concentrations were referenced to a solution which was saturated with oxygen by oxygen bubbling. Molecular oxygen is reported to have a concentration of 9.1×10^{-3} M in benzene at 1 atm [18]. The three oxygen concentrations used in the fluorescence lifetime estimates were (1) saturated solution (100% of 9.1×10^{-3} M), (2) solutions which were equilibrated with room air (21% of 9.1×10^{-3} M) and (3) helium-flushed solutions (considered to have no oxygen present). In general, quenching of singlet states by molecular oxygen occurs at a rate of $(1 - 3) \times 10^{10}$ M^{-1} s^{-1} in benzene [18, 19]. Using the quenching rate of oxygen as 3×10^{10} M^{-1} s^{-1} and the measurements of the emission intensity of three aryl phosphine solutions at the different oxygen concentrations, the natural fluorescence lifetime τ_f can be calculated by the Stern–Volmer relationship, $I/I_{O_2} = 1 + k_q\tau_f[O_2]$. I and I_{O_2} are the intensity of the non-quenched and quenched emissions. A linear plot of I/I_{O_2} *versus* $[O_2]$ gives a slope equal to $k_q\tau_f$. The oxygen concentration was plotted as the percentage of the saturated concentration. Figure 1 shows a plot of I/I_{O_2} *versus* percentage of saturated oxygen concentration for $MePh_2P$ and $Ph_2PCH_2PPh_2$. The fluorescence lifetimes estimated by this method were doubled for the diphosphines to compensate for the quenching of two chromophores in one molecule. The fluorescence lifetime of diphenylamine determined by this method was calculated to be 3.5 ns compared with the recently reported value of 3.2 ns determined by time-correlated single-photon counting using an Ortec 9200 nanosecond fluorescence spectrometer [20].

2.4. *Excitation spectra*

A Varian SF-330 spectrofluorometer was used to record the detailed excitation spectra of the fluorescent emissions at room temperature. The excitation spectra were checked at 77 K using the instrumentation described. The excitation monochromator was manually changed by 5 nm increments and the emission reading from the maximum emission wavelength of the sample was recorded. The excitation characteristics at 77 K taken with the described instrumentation appeared to be the same as the room temperature spectrum recorded on the Varian SF-330 spectrofluorometer. The excitation spectrum from the SF-330 spectrofluorometer is autocorrected for source and monochromator wavelength dependence. The concentrations of the samples were varied from about 10^{-3} to about 5×10^{-6} M and the aryl phosphines only showed emission at the higher concentrations. The emission spectra of the aryl phosphines were all recorded with excitation at 313 nm. The emission spectra of the phosphine oxides were taken with excitation at 265 nm.



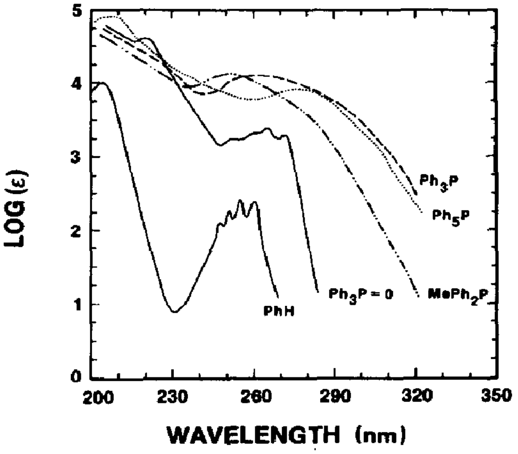


Fig. 1. Stern–Volmer oxygen quenching analysis, $I/I_{O_2} = k_q\tau_f[O_2]$: □, $MePh_2P$; ■, $Ph_2PCH_2PPh_2$. The values used to calculate τ_f were $k_q = 3 \times 10^{10}$ M^{-1} s^{-1} and [O_2] (saturated) = 9.1×10^{-3} M [18, 19]. I and I_{O_2} are the intensities of the non-quenched and oxygen-quenched emissions respectively.

Fig. 2. Comparison of absorption spectra of benzene, $Ph_3P{=}O$, Ph_3P, $MePh_2P$ and Ph_5P in cyclohexane [1, 3, 21].

3. Results

The UV absorption spectra of Ph_3P and $MePh_2P$ taken in cyclohexane are shown in Fig. 2. The structure of the absorption spectra of the diphosphine series, $Ph_2P(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$), is essentially identical with the absorption spectrum of $MePh_2P$. The diphosphines show extinction coefficients ϵ at the maximum absorption peak (251 nm) of almost exactly twice that of $MePh_2P$, *i.e.* for $MePh_2P$ $\epsilon = 9.0 \times 10^3$ M^{-1} cm^{-1}, for $Ph_2PCH_2PPh_2$ $\epsilon = 18.2 \times 10^3$ M^{-1} cm^{-1} and for $Ph_2P(CH_2)_2PPh_2$ $\epsilon = 18.5 \times 10^3$ M^{-1} cm^{-1}. However, the extinction coefficients of the diphosphines vary considerably at the longer wavelengths (greater than 290 nm). The extinction coefficients of the phosphines measured in benzene at 313 nm are shown in Table 1.

TABLE 1

Absorption and emission properties of diphosphines $Ph_2P(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$) compared with Ph_3P and $MePh_2P$

Compound	*Absorption* $\epsilon(313)$[a] (M^{-1} cm^{-1})	*Relative fluorescence* ϕ[b]	*Fluorescence* τ_f[c] (ns)	*Phosphorescence* τ_p[d] (ms)
Ph_3P	450	(2.0)[e]	2.0	17
$MePh_2P$	65	(1.0) (reference)	2.5	40
$Ph_2PCH_2PPh_2$	151	(0.17)	0.7	29
$Ph_2P(CH_2)_2PPh_2$	242	(0.60)[e]	1.2	38
$Ph_2P(CH_2)_3PPh_2$	161	(0.38)	1.0	43
$Ph_2P(CH_2)_4PPh_2$	171	(0.68)	1.8	42
$Ph_2P(CH_2)_5PPh_2$	175	(0.74)	2.0	45
$Ph_2P(CH_2)_6PPh_2$	170	(0.78)	2.0	46

[a] Extinction coefficient at 313 nm measured in benzene.

[b] Relative quantum yields at 298 K in comparison with $MePh_2P$.

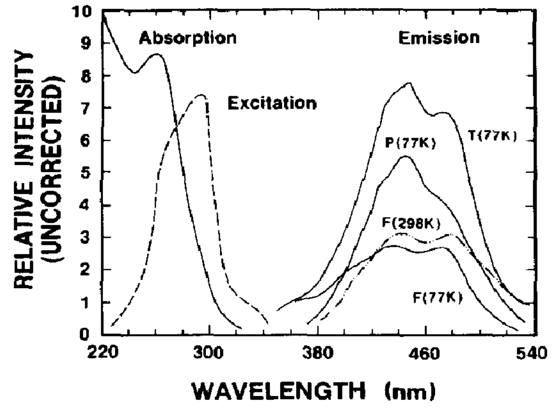
[c] Fluorescence natural lifetime determined by oxygen quenching at 298 K. The value for diphosphines was doubled to account for the statistical quenching of the two chromophores.

[d] Phosphorescence natural lifetime determined in EPA glass at 77 K.

[e] Quantum yields of Ph_3P and $Ph_2P(CH_2)_2PPh_2$ reported as 3.3×10^{-3} and 8.6×10^{-4} respectively in ref. 14.

Table 1 also summarizes some of the emission properties of the aryl phosphines studied. The excitation and emission spectra of Ph_3P at 77 K are shown in Fig. 3. The excitation and emission spectra of $MePh_2P$ and the diphosphine series at 77 K are essentially the same as that of Ph_3P. Emission from the aryl phosphines is also observed at room temperature. The emission at room temperature is categorized as fluorescence since the lifetime in the nanosecond range (Table 1), determined by oxygen quenching, is too short for phosphorescence. The emission at room temperature in benzene is shifted by 5 - 10 nm to longer wavelengths than the fluorescence spectrum at 77 K, but it has an identical shape (Fig. 3). The uniformity of the oxygen quenching over the entire emission band at room temperature indicates that the emission is coming from only one excited state. Thus the entire emission spectrum is fluorescence, phosphorescence not being observed at room temperature. Only minor differences are observed in the fluorescence spectra of Ph_3P and $MePh_2P$. The fluorescent emission spectra at room temperature of the diphosphines are identical with that of $MePh_2P$. However, the quantum yields of emission and lifetimes of the diphosphines do differ (Table 1).

The excitation spectrum shown in Fig. 3, which is representative of all the aryl phosphines studied, is an approximation. The excitation spectrum was very difficult to measure since the emission is very weak and was only observed for fairly concentrated solutions (about 10^{-4} M or more) excited at longer wavelengths than where maximum absorption is shown in the UV (250 - 260 nm). When a phosphine solution was made to show less than approximately 0.10 absorbance (about 10^{-5} M) at 250 nm no emission over



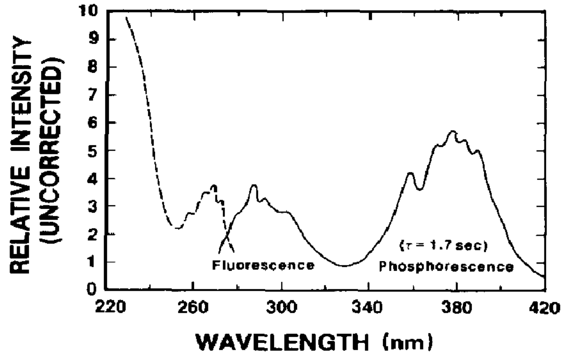


Fig. 3. Excitation and emission spectra of Ph_3P in EPA at 77 K and in benzene at 298 K (T, total emission spectrum; P, phosphorescence spectrum with $\tau_0 = 17$ ms; F, fluorescence spectrum). Only fluorescence is observed in benzene at 298 K. The relative intensities of the 298 and 77 K fluorescence emissions are normalized to approximately the same relative intensity for comparison only. The absorption spectrum is indicated for comparison with the excitation spectrum.

Fig. 4. Excitation (– – –) and emission (——) spectra of $Ph_3P{=}O$ in EPA at 77 K. The excitation spectrum was taken by monitoring the fluorescence at 290 nm. The emission spectrum was taken with excitation at 265 nm.

background was observed. Many times an impurity emission was observed when the more dilute solutions were excited at 250 - 260 nm. The impurity emission was identified as the emission spectrum of the phosphine oxide. The detailed excitation and emission spectra as well as the phosphorescence lifetimes of $Ph_3P{=}O$ and $MePh_2P{=}O$ were recorded in order to identify the impurity emission observed from the phosphines positively. The data for $Ph_3P{=}O$ are shown in Fig. 4. The $MePh_2P{=}O$ data are very similar to those for $Ph_3P{=}O$. The phosphorescent lifetime of $MePh_2P{=}O$ is 1.4 s. The emission spectrum of $Ph_3P{=}O$ has been reported in the literature [10] but only in a vague tabular form.

4. Discussion

In comparing the emission spectrum of $Ph_3P{=}O$ (Fig. 4) with the previous spectra reported in the literature for Ph_3P [8 - 12], it becomes obvious that the conflicting emission spectra reported for Ph_3P have been caused by contamination of the phosphine with the phosphine oxide. In fact, the spectrum reported in 1970 [8] as Ph_3P is actually the emission spectrum of $Ph_3P{=}O$. Confusing the matter further is the fact that the spectrum was labeled with the lifetime of Ph_3P as measured by McClure [12]. The mistake of identifying the $Ph_3P{=}O$ spectrum as Ph_3P could easily have been made since no lifetime measurements were taken and Ph_3P does not emit strongly when excited at 260 nm where its maximum absorption occurs. $Ph_3P{=}O$ gives a rather strong emission with excitation at 260 nm compared with Ph_3P. The erroneous spectrum reported for Ph_3P [8] is still often quoted [22] since it is the only detailed spectrum of Ph_3P appearing in literature published in English. Using the intersection of the excitation and emission spectra shown in Fig. 3, the lowest excited singlet energy E_s is approximately 79 - 82 kcal mol^{-1}. The lowest triplet energy E_T is only slightly less at 75 - 77 kcal mol^{-1}.

The excitation spectra of $Ph_3P{=}O$ and $MePh_2P{=}O$ show the usually observed identical relationship with the absorption spectra. The anomaly of the excitation spectra of the aryl phosphines (Fig. 3) in comparison with the absorption spectra (Fig. 2) indicates that a lower energy excited state exists than that associated with the maximum absorption at 250 - 260 nm. The maximum emission appears to occur with excitation between 290 and 310 nm. Therefore, there must be a less intense absorption band with a maximum at about 300 nm hidden under the broad rather intense band shown in the absorption spectra (Fig. 2). Higher order excited states associated with the absorption bands at shorter wavelengths apparently do not favorably decay to the lowest excited states.

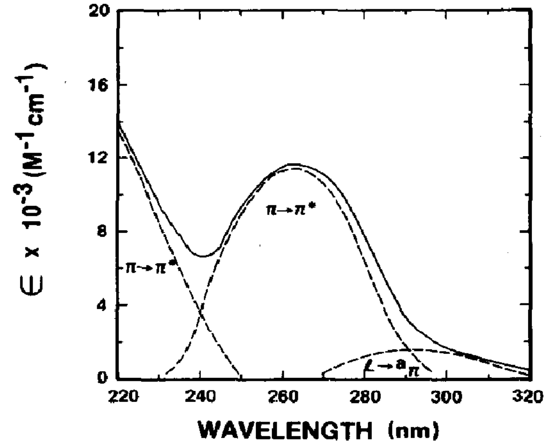
The emission spectra of the aryl phosphines are also somewhat anomalous in that there is little distinction or separation between fluorescence and phosphorescence. The first excited singlet S_1 and triplet T_1 states must be very close in energy to account for the large overlap of the phosphorescent and fluorescent emissions. The very small singlet–triplet splitting observed for the aryl phosphines suggests that the orbitals involved in the electronic transition occupy different regions of space. Thus, the singlet–triplet splitting of the aryl phosphines indicates that the lowest excited state is an n,π^* state and that the non-bonding electrons of the phosphorus have essentially no interaction with the phenyl π system in the ground state. There appears to be a slight difference in the shape of the two emissions yet the maxima occur at approximately the same wavelengths. A possible explanation for this apparent anomaly is that a considerable portion of the phosphorescence spectra could be due to a delayed fluorescence. Delayed fluorescence can arise if the singlet–triplet energy difference is small and a thermally induced equilibrium between the states is established. The delayed fluorescence ($S_0 + h\nu \rightarrow S_1 \rightarrow T_1 \rightarrow S_1 \rightarrow S_0 + h\nu'$), which would be kinetically controlled, would have a much longer lifetime than the normal fluorescence. The lifetime of the singlet is much shorter than the lifetime of the triplet, and therefore the lifetime of the delayed fluorescence would be nearly equal to the lifetime of the triplet state.

The shape of the emission spectra of the aryl phosphines indicates a substantial difference in geometry between the ground state and the excited state. The difference in energy between the two definite vibrational peaks that are observed in the fluorescence spectra (Fig. 3) corresponds to 1440 cm^{-1}. Such a vibrational pattern would be expected for emission from an excited state if the transition involves the P—Ph group. Aromatic phosphorus compounds show a strong very sharp IR peak near 1440 cm^{-1} in compounds in which a phosphorus atom is attached directly to the benzene ring [23]. The type of emission described is very similar to that of carbonyl compounds where the n → π* electronic transition is the emitting excited state. The phosphorescence of acetophenone and benzophenone shows a vibrational pattern that is characteristic of the C=O vibrational stretch in S_0 [24]. However, the electronic transition n → π* is considered to be a forbidden transition since the lone electron pair orbital of the oxygen is orthogonal to the π system. The observed transition probability is believed to be due to the mixing of the nuclear vibrational motion with the electronic structure of the molecule (vibronic states). For carbonyl compounds the out-of-plane vibration of the C=O bond is thought to provide a mechanism for the n → π* electronic transition. Since the electronic transition is localized on the C=O group, excess vibrational energy is left on the carbon and oxygen atoms. It appears that vibronic coupling is also responsible for the electronic transition in the aryl phosphines. The lone electron pair of phosphorus in Ph_3P would have considerable s character since the pyramidal valence angle is 103° [25]. The largest valence angle observed for aryl phosphines is only 109.5° [26], indicating an sp^3 hybridization of the lone electron pair orbital of the phosphorus. This would place the lone electron pair orbital orthogonal to the phenyl π system, and thus the transition would be forbidden. However, in the extreme case of an in-plane vibration causing an sp^3 (pyramidal) → p (planar) rehybridization of the lone electron pair orbital, the electronic transition would become allowed. Thus the vibronic coupling of aryl phosphines could be postulated to be very similar to that of carbonyl compounds and the emission spectra would be expected to show vibrational structure of the P—Ph stretching mode of S_0 [27]. Rather than the n → π* classification given to the carbonyl compounds, the $l \rightarrow a_\pi$ terminology used by Kasha and Rawls [28] for aromatic amines appears to be more appropriate. The lone pair orbitals l have the possibility of bonding relative to the π electron system of the molecule, depending on the bonding angle and twist angle of the phenyl group relative to the phosphorus atom. The l orbital corresponds to a non-planar or twisted lone pair orbital and the orbital to which the electron is promoted is an antibonding orbital a_π of π origin. In the limiting cases the $l \rightarrow a_\pi$ transition could have characteristics of the n → π* transition (orthogonal orbitals) or the π → π* transition (planar molecule with complete p–π conjugation).

With the research reported in the literature to date, it is apparent that the electronic transition assignments made for the aryl phosphines are contradictory. No assignment is in agreement with the expected characteristics of either limit of assignment of the $l \rightarrow a_\pi$ transition, the n → π* or the π → π* transition. For example, an n → π* transition has a typical extinction coefficient of 10 - 500 M^{-1} cm^{-1} while the π → π* transition has an extinction coefficient for allowed transitions of 10^4 - 10^5 M^{-1} cm^{-1} [19, 24, 28]. The 260 nm region of the Ph_3P spectrum (Fig. 2) has an extinction coefficient of about 10^4 M^{-1} cm^{-1}. The high extinction coefficient favors the π → π* assignment; however, we know from other research that there is very little effective lone electron pair conjugation with the phenyl system in the ground state [21]. However, if the n → π* assignment is correct, why is the extinction coefficient reflective of a highly allowed transition?

On the basis of the results of this study, there is sufficient evidence to suggest more reasonable assignments of the electronic transitions of the aryl phosphines than have been previously suggested in the literature. The absorption at 220 nm and the broad intense absorption band at about 260 nm are assigned to π → π* localized benzene transitions while a lower energy $l \rightarrow a_\pi$ transition of n → π* character is associated with a low intensity absorption band centered around 290 - 310 nm, which is obscured by the more intense π → π* transition absorption band centered at about 260 nm (Fig. 5). The large increase in the intensity and loss of vibrational structure of the π → π* transition at 260 nm of the phenyl system in comparison with benzene are attributed to the breakdown in symmetry of the benzene ring by substitution of the phosphorus atom on the phenyl ring as well as to an inductive effect. The absorption spectra of many monosubstituted benzene systems show shifts of the benzene absorption to longer wavelengths with an increase in band intensities and a reduction in the amount of vibrational structure [23]. A specific example that applies to the Ph_3P system is the recently reported absorption spectrum of Ph_5P [29]. Ph_5P has no lone electron pairs on the phosphorus and would probably be expected to show the same type of absorption spectrum as $Ph_3P{=}O$. However, the absorption spectrum of Ph_5P is more like that of Ph_3P. A comparison of the absorption spectra of benzene, $Ph_3P{=}O$, Ph_3P and Ph_5P is shown in Fig. 2. It appears that the increase in intensity of the π → π* transitions in the phenyl groups at about 210 nm and about 260 nm is due to perturbation of the benzene ring through symmetry and inductive effects rather than conjugation of the lone electron pair in Ph_3P. Some of the evidence for the assignment of an $l \rightarrow a_\pi$ transition of essentially n → π* character has been discussed. A small singlet–triplet splitting is consistent with an n → π* transition. The vibrational structure of the emission spectra is consistent for emission from an n → π* excited state transition in which the electronic transition leaves vibrational energy which is dissipated in a P—Ph vibration. The phosphorescence lifetimes are also of the nature of an n → π* transition. The phosphorescence lifetime of Ph_3P is 17 ms while those of benzene and $Ph_3P{=}O$ are 4.1 s and 1.7 s respectively [11, 18]. The excitation spectra indicate a hidden absorption band centered around 290 - 310 nm which is assigned to the $l \rightarrow a_\pi$ transition. A much lower extinction coefficient (100 - 200 M^{-1} cm^{-1}) which would be associated with the absorption band is consistent with an n → π* transition.

The $l \rightarrow a_\pi$ (n → π* character) electronic transition assignment is further substantiated by the results of the absorption and emission study of the diphosphine series $Ph_2P(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$) (Table 1). The structure of the absorption spectra measured in cyclohexane of the diphosphine series is essentially identical with that of $MePh_2P$. The diphosphines show extinction coefficients at the maximum absorption peak (251 nm) of exactly twice that of $MePh_2P$. This result is what would be expected of two



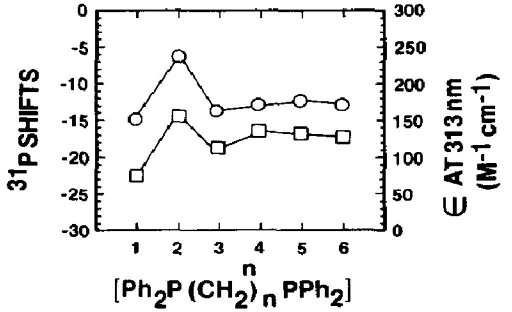
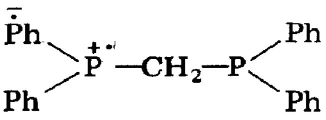


Fig. 5. Illustration of the electronic transition assignments of Ph_3P. This illustration depicts the electronic transitions of the aryl phosphines showing the obscured $l \rightarrow a_\pi$ transition.

Fig. 6. Comparison of ^{31}P shifts (□) and extinction coefficients ϵ (○) at 313 nm of the diphosphine series $Ph_2(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$). The abscissa represents the number of $—CH_2—$groups. The ^{31}P chemical shifts were taken from ref. 29.

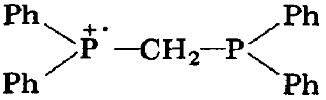
independent chromophores in one molecule. However, the extinction coefficients of the diphosphine are not twice the extinction coefficient of $MePh_2P$ at the longer wavelengths (greater than 290 nm). The extinction coefficients of the diphosphines shown in Table 1 at 313 nm vary considerably. It is striking that $Ph_2P(CH_2)_2PPh_2$ appears to deviate from any trend that might be present. This same deviation is observed in ^{31}P chemical shifts. In fact, the extinction coefficients at 313 nm of the diphosphines follow the same pattern as their ^{31}P chemical shifts [30]. Figure 6 shows the ^{31}P chemical shifts on the left-hand ordinate and the extinction coefficients on the right-hand ordinate with the abscissa representing the number of $—CH_2—$ groups separating the phosphorus atoms. No adequate explanation has been given for the observed ^{31}P chemical shifts [30] and this study offers no new theories as to the exact nature of the observed pattern in the ^{31}P chemical shifts and extinction coefficients at 313 nm. However, it is known that ^{31}P chemical shifts are sensitive to minor changes in geometric structure and spatial orientation of the lone electron pair orbital. The extinction coefficient at 313 nm is probably reflective of the hidden absorption band assigned to an $l \rightarrow a_\pi$ transition ($n \rightarrow \pi^*$ character). If this is the case, the extinction coefficient at 313 nm would also be very sensitive to minor changes in geometric structure and spatial orientation of the lone electron pair orbital. The constancy and additivity of the extinction coefficient at 250 nm (twice that of $MePh_2P$) of the diphosphine series in comparison with the variance in the 313 nm extinction coefficients (Fig. 6) is a further indication of the correct electronic transition assignments of a $\pi \rightarrow \pi^*$ transition centered on the phenyl rings at 250 nm and of an $l \rightarrow a_\pi$ ($n \rightarrow \pi^*$ character) associated with a hidden absorption band at about 300 nm.

Since the electronic transitions of the diphosphines appear to be the same as those of $MePh_2P$, the emission spectra would also be expected to be similar to that of $MePh_2P$. The emission spectra of the diphosphines at 77 K appear to be identical with that of $MePh_2P$. The measured phosphorescence natural lifetimes of the diphosphines are also very similar to that of $MePh_2P$ (Table 1). The fluorescent emission spectra at room temperature of the diphosphines are also identical with that of $MePh_2P$; however, the quantum yields of emission and lifetimes of the diphosphines at room temperature appear to be dependent on the number of $—CH_2—$ groups separating the phosphine lumophores (Table 1). The lifetime and the quantum yield of emission are reduced considerably as the distance between the lumophores is reduced. $Ph_2P(CH_2)_2PPh_2$ shows an anomaly in the trend. The dependence of the lifetime and quantum yield of emission on the number of $—CH_2—$ groups suggests an intramolecular quenching process. No new distinguishable emissions in the diphosphines exhibiting the lower quantum yields of fluorescent emission were observed and no photolysis experiments on the diphosphines were performed to identify photoproducts that might be associated with an intramolecular quenching process. However, as a conjecture, an interaction between an excited state phosphine and a ground state phosphine similar to that observed in the mass spectrometry of the diphosphines [31] could be envisioned. The idea has some merit since the charge transfer character of the electronically excited state of the phosphine



n → π^* character

would be similar to the radical formed by electron impact in the mass spectrometer



The very small singlet–triplet splitting of the diphosphines is consistent with an excited state of a biradical nature. The phosphorus would become a strong electrophile in the electronically excited state in contrast with a nucleophile in the ground state.

5. Conclusions

5.1. Electronic transition assignments

The primary conclusion from the study of the photophysical properties of the aryl phosphines Ph_3P, $MePh_2P$ and the diphosphine series

$Ph_2P(CH_2)_nPPh_2$ (from $n = 1$ to $n = 6$) has been an improved classification of their electronic transition states. The lowest energy excited electronic state of the aryl phosphines has been assigned to an $l \rightarrow a_\pi$ transition, signifying an electron transfer from a lone electron pair orbital l on phosphorus to an antibonding π orbital on a phenyl π group. The $l \rightarrow a_\pi$ transition is of an $n \rightarrow \pi^*$ character in contrast with aryl amines which also can be classified as having an $l \rightarrow a_\pi$ electronic transition but show characteristics similar to $\pi \rightarrow \pi^*$ transitions. Thus aryl phosphines exhibit photophysical properties more closely associated with carbonyl compounds ($n \rightarrow \pi^*$) than aryl amines. The $l \rightarrow a_\pi$ ($n \rightarrow \pi^*$ character) electronic transition in the aryl phosphines is associated with a hidden low intensity absorption band at 290 - 300 nm. The maximum absorption band at 250 - 260 nm has been assigned to a $\pi \rightarrow \pi^*$ transition centered on the phenyl π system (see Fig. 5).

5.2. *Emission spectra of triphenylphosphine*

The emission spectrum of Ph_3P reported [8] in the literature is not correct. The spectrum reported is identical with that of $Ph_3P{=}O$ and must have been mistakenly identified because of some phosphine oxide impurity. The erroneous spectrum has caused considerable confusion and misinterpretations to persist in the literature relating to Ph_3P.

5.3. *Excited state energies*

The electronic excited state energies of the aryl phosphines studied show very little difference. The lowest excited singlet energy of the aryl phosphines studied is calculated to be 79 - 82 kcal mol^{-1} with the triplet energy being estimated to be 75 - 77 kcal mol^{-1}.

5.4. *Diphosphines*

An intramolecular quenching process of room temperature fluorescence appears to be operative in the diphosphines $Ph_2P(CH_2)_nPPh_2$ for $n \leqslant 3$. The nature of the intramolecular quenching was not determined.

5.5. *The effect of metal coordination*

The electronic transition ($l \rightarrow a_\pi$) of the aryl phosphines is enhanced by coordination to copper(I), and the phosphine–copper(I) electronic transition has been classified as $\sigma,d \rightarrow a_\pi$. The photophysical properties of these coordination compounds have been determined as an extension of the work reported here [32].

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