# Investigation of Singlet → Triplet Transitions by the Phosphorescence Excitation Method. III. Aromatic Ketones and Aldehydes

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**Abstract:** The single → triplet absorption spectra of 16 photochemically active aromatic ketones and aldehydes have been investigated by the phosphorescence excitation method. Both n,π and π,π triplet states have been located in a number of molecules. The relation between our experimental findings and a recent theoretical interpretation of intersystem-crossing mechanisms in carbonyl compounds is discussed. The intensity of singlet → triplet transitions in carbonyl compounds is examined theoretically, and it is predicted that the $S \rightarrow T_{\pi,\pi}$ transitions in aromatic compounds should be enhanced by the presence of the $>C{=}O$ substituent. This prediction is experimentally verified with several examples. Within the accuracy of our experiments, there was no external heavy atom effect on the intensity of the $S \rightarrow T_{n,\pi}$ transitions, although the addition of ethyl iodide to the solvent did enhance the somewhat weaker $S \rightarrow T_{\pi,\pi}$ transitions by about a factor of 2. This difference in sensitivity to external heavy atoms provides a useful criterion for distinguishing $S \rightarrow T_{n,\pi}$ and $S \rightarrow T_{\pi,\pi}$ transitions. The relation of the spectroscopic results to the interpretation of the photochemical properties of these molecules is discussed.

Interest in the triplet-state properties of organic molecules has been considerably stimulated by recent developments in a number of areas including photochemistry,[3-6] photobiology,[7-9] the theory of spin-orbit coupling of singlet and triplet states,[10,11] and the theory of radiationless transitions.[12-14]

In a number of photochemical studies, particularly those involving aromatic ketones and aldehydes, the excited-state chemical reactions often proceed from the triplet state.[3-6] These photochemical studies have served to emphasize the important role which the lowest triplet state plays in the excited-state chemistry of these molecules and prompted several attempts to correlate reactivity with the nature of the lowest triplet state.[4-6] Although these efforts have been generally successful, there are some notable "anomalies." Apparently factors in addition to the nature of the triplet state are important, and more photochemical data and spectroscopic information on triplet states appear to be required.

Beyond the consideration of the relation between photochemical activity and nature of the lowest excited triplet state, there is the question of what the mechanisms are by which the lowest triplet state is populated following excitation of the molecule to some higher lying excited singlet state.

Recent developments in the theory of radiationless transitions have provided us with a partial understanding of these processes, but at the same time these studies have raised new questions regarding the nature and location of triplet states which lie *above* the lowest triplet state.[12-14] Until now, we have had little information regarding the nature and location of these higher lying triplet states. Consequently, it has not been possible to determine just how important a role these high-lying triplet states play in determining rates of intersystem crossing.

The investigation of radiationless transitions and mechanisms of intersystem-crossing processes has necessarily involved a consideration of spin-orbit interaction in aromatic carbonyl compounds. This, in turn, has led to some interesting predictions regarding the intensity of singlet → triplet transitions and the effect which heavy atom perturbers have on these transitions.[15] Again, because of a lack of experimental data on the singlet → triplet (S→T) absorption spectra of aromatic carbonyl compounds, these predictions remain unchecked.

Until recently, most of our information concerning the lowest triplet state of molecules has been obtained from studies of triplet → singlet emission spectra.[15] While very convenient, this method allows the position of only the *lowest* triplet state to be determined. To locate triplet states which lie *above* the lowest triplet state, or to investigate the vibrational structure of the lowest excited triplet state, some type of absorption technique is required. Because singlet → triplet transitions are very weak, perturbation techniques (paramagnetic molecules,[16] inter- and intramolecular heavy atom perturbers[17,18]) are generally used to enhance the S→T transition probability. But even with these perturbation techniques, long path lengths and high concentrations are required to carry out direct absorption measurements on S→T transitions.[18] With these latter conditions, impurity absorption frequently causes difficulties.

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Rather than use a direct absorption technique, we have made use of the phosphorescence excitation method, which we described briefly in an earlier note,[19] to investigate the singlet → triplet absorption spectra of various aromatic ketones and aldehydes.[20,21] The work reported here was undertaken to: (i) determine the location and assignment of not only the lowest triplet state of the aromatic ketones and aldehydes, but higher lying triplet states as well; (ii) investigate external heavy atom effects on both $S \rightarrow T_{n,\pi}$ and $S \rightarrow T_{\pi,\pi}$ transitions; (iii) determine the effect of the $>C{=}O$ group on the intensity of the $S \rightarrow T_{\pi,\pi}$ transitions in aromatic ketones and aldehydes; and (iv) further develop the phosphoresence excitation method for determination of S→T absorption spectra.

## Experimental Section

**1. Discussion of the Phosphorescence Excitation Method.** It is perhaps not immediately obvious that an *indirect* method for measuring absorption spectra can be superior, in many respects, to a *direct* method. We shall therefore briefly discuss the principle of the phosphorescence excitation method as it applies to the measurement of singlet → triplet absorption spectra. From this analysis the advantages of this method will become evident.

In order to measure a singlet → triplet absorption spectrum by the phosphorescence excitation method, a sample is excited by a monochromatic beam of light of wavelength $\lambda$ and of intensity $L_0$. If the intensity of the light which passes through the sample is $L$, the rate, $N$, at which photons are absorbed by a sample is

$$N = (L_0 - L) \qquad (1)$$

which by Beer's law is

$$N = L_0[1 - \exp(-2.3\epsilon Ct)] \qquad (2)$$

where $\epsilon$ is the molar extinction coefficient of the sample at the wavelength of excitation $\lambda$, $C$ is the concentration of the light-absorbing species, and $t$ is the sample thickness. If the product $2.3\epsilon Ct$ is small compared to 1, as it is in the case of very weak transitions, the exponential may be expanded. With this expansion, $N$ is given by

$$N \simeq L_0 2.3\epsilon Ct \qquad (2.3Ct \ll 1) \qquad (3)$$

Now $N$ represents the number of quanta absorbed per second. Alternatively, it is the rate at which molecules are excited to some electronically excited state. If the excitation is restricted to wavelengths within the singlet → triplet absorption region, $N$ represents the rate at which triplet-state molecules are generated. Note that under these conditions $N$ varies linearly with $\epsilon$, the molar extinction coefficient. In principle, any method which measures the rate at which triplet-state molecules are generated can be used to determine singlet → triplet absorption spectra. Triplet-state sensitized chemical reactions or electron spin resonance could, for example, be used, but the most convenient method for detecting the production of triplet state molecules is to measure the intensity of phosphorescence emission which results from the generation of triplet-state molecules.

When a sample is excited in a singlet → triplet absorption band, the intensity of the emitted phosphorescence, $I_{\text{phos}}(\lambda)$, will be proportional to $N$, or in terms of the parameters of interest

$$I_{\text{phos}}(\lambda) = NXq = L_0(\lambda)\epsilon CtXq = L_0(\lambda)\epsilon\beta \qquad (4)$$

where $q$ is an apparatus constant and $X$ is the fraction of triplet-state molecules which phosphoresce. It is assumed in writing down this equation that internal conversion within the triplet manifold is rapid compared to other processes which tend to depopulate triplet states.

It is clear from eq 4 that when $\lambda$ is restricted to the singlet → triplet absorption region, a measurement of $I_{\text{phos}}(\lambda)$ as a function of wavelength of the exciting light will, within a factor $L_0\beta = L_0 \times (qCtX)$, be identical with the singlet → triplet absorption spectrum of the sample. Since $\beta$ for a given molecule is a constant independent of the wavelength of excitation, relative singlet → triplet absorption spectra can be determined if the relative photon distribution of the excitation source is known. As we have demonstrated elsewhere, absolute values of the extinction coefficient for singlet → triplet transitions can also be determined, provided intersystem-crossing quantum yields are known.[20]

With this discussion of the principle of the method, some of the advantages of the phosphorescence excitation method for investigating S→T transitions are now evident.

(i) **High Sensitivity.** Since intense monochromatic light may be used to excite the sample, and since weak phosphorescence emission can be detected, it is possible to detect very sensitively extremely weak S→T transitions by the phosphorescence excitation method.

In general, only a very small fraction of the exciting light has to be absorbed by the sample in the excitation method (on the order of the ratio of the sensitivity of the photomultiplier to the intensity of the exciting light, reduced by a photomultiplier collection efficiency factor), whereas in a direct absorption measurement, a substantial fraction (order of, *e.g.*, 0.1%) of the light has to be absorbed. By alternately chopping the exciting and the emitted light in a conventional phosphoroscope arrangement, problems connected with separating the exciting light from the emitted light are minimized.

(ii) **Impurity Effects Minimized.** In order for an impurity to affect an excitation measurement, it must absorb light in the appropriate region and lead to the *proper* type of phosphorescence. This immediately eliminates complications due to many impurities which would ordinarily complicate a direct absorpton measurement and allows significant measurements to be carried out on samples which are not as pure as those required for direct absorption measurements.

(iii) **Impurity Effects Easily Evaluated.** With the exception of the high sensitivity, this is perhaps the most important feature of the phosphorescence excitation method. If we consider measurements on compounds dissolved in some glassing solvent, there are only two types of impurities which are likely to be important.

(a) The first type involves impurities which have strong absorption bands in the same region as the S→T absorption of the sample and phosphoresce in the same region as the sample. Unless the phosphorescence spectrum of the impurity is identical with that of the sample, both spectrally and in lifetime, this type of impurity can easily be detected by examining the *phosphorescence spectrum* of the sample when it is excited at different, fixed wavelengths. If the phosphorescence spectra obtained in this way are identical with the true sample phosphorescence spectrum, regardless of the wavelength of excitation, it may be taken as established that this type of impurity is probably absent.

(b) The second type involves impurities which have a strong absorption band below the lowest S→S absorption band of the sample, and a lowest triplet state which lies above the lowest triplet state of the sample. This type of impurity can absorb light in a S→S transition, undergo intersystem crossing to its lowest triplet state, and sensitize the sample phosphorescence by triplet–triplet energy transfer. As this type of impurity effect depends upon energy transfer to the sample, it becomes *relatively* less effective when the concentration of the sample is reduced. Therefore, if the *shape* of the *phosphorescence excitation spectrum* remains unaltered when the concentration of the sample is decreased, this may be taken as evidence against the presence of this type of impurity.

These simple experimental tests provide very useful criteria for establishing the authenticity of phosphorescence excitation spectra, which one does not have in direct absorption measurements.

(iv) **The Absorption Spectra of Very Small Samples May Be Easily Measured.** In a direct absorption measurement, the sample must interrupt a major portion of the incident light beam, and therefore relatively large samples are required, or microspectrophotometric techniques must be used if small samples are to be studied. In the phosphorescence excitation method, the sample does not have to interrupt a major fraction of the exciting light; therefore, measurements may be carried out on quite small samples.

A potential problem with the determination S→T absorption by the phosphorescence excitation method arises from the fact that the light transmitted by the excitation monochromator may not be completely monochromatic. If, for example, scattered light of a

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wavelength shorter than the principal band is passed by the monochromator, it is possible that this short wavelength light will be absorbed in a strong S→S transition and generate more triplet states than the weakly absorbed main excitation beam. By comparing excitation spectra taken with and without the appropriate short wavelength cutoff filter, the importance of stray, short wavelength light can easily be assessed and cutoff filters can be used to eliminate it. With the monochromator and filter system which we used, we encountered no problems with short wavelength stray light.

Because of its high sensitivity, insensitivity to impurities, the ease with which impurity effects can be evaluated, and its applicability to small samples, the determination of singlet–triplet absorption spectra by the phosphorescence excitation technique is reduced to an almost routine measurement.

**2. Experimental Apparatus.** Phosphorescence excitation spectra were obtained with a conventional phosphoroscope by exciting the samples with light from a 450-w xenon arc lamp which was monochromatized by passing through a Bausch and Lomb 1350 grooves/mm monochromator (64 A/mm dispersion) and appropriate cutoff filter and optical system. With the exception of the single-crystal measurements where higher resolution was warranted, the slits on the excitation monochromator were 0.5 mm. The spectral distribution of the photon output was determined by placing a fluorescent fluorescein solution *at the sample position* and monitoring the fluorescence intensity. These results are shown in Figure 1. Unless otherwise specified, the excitation spectra have not been corrected for the spectral distribution of the exciting light, as the exciting light photon distribution was relatively flat over the region of interest. The phosphorescence emission was monitored at right angles to the exciting light after passing through a chopper and a second Bausch and Lomb monochromator, or filter system, to a 1P-28 photomultiplier operated at 900 v. Relative triplet-state lifetimes were determined by measuring the variation of the phosphorescence intensity with the chopper speed.

**3. Samples.** Two types of samples were used in the phosphorescence excitation measurements: compounds dissolved in glassing solvents and crystalline samples. With the former type of sample, the compounds were dissolved in a glassing solvent system, placed in a 7-mm Pyrex tube, and then into the phosphoroscope dewar which was cooled to 77°K by liquid nitrogen. In order to obtain high senstivity, sample concentrations were typically on the order of 0.1 *M*. With a few of the ketones which were particularly insoluble, precipitation occurred when the glasses were warmed from 77°K, but in general there was no evidence for precipitation during the initial cooling step.

The following two solvent systems were used in the solution studies: (i) ether, ethanol, and toluene in a ratio of 2:1:1 (EET), and (ii) ether, ethanol, toluene, and ethyl iodide in a ratio of 2:1:1:2 (TEEE), respectively. Through the use of the first solvent system, the S→T absorption spectra of the unperturbed molecules were obtained. Through the use of the second solvent system it was possible to study the effect of external heavy atoms on the intensity of S→T transitions.

In order to obtain better resolved S→T absorption, spectral measurements were also carried out on crystalline samples of *p,p'*-dibromobenzophenone, 2,4'-dibromoacetophenone, and 4'-bromoacetophenone. For these studies, crystals of these compounds were grown from solutions to which we purposely added small concentrations of naphthalene. The crystals which grew from these solutions consequently contained a low concentration of naphthalene, and as a result of triplet–triplet energy transfer, only the naphthalene phosphorescence was observed from these doped samples. The singlet → triplet absorption spectra of these doped crystals were then determined by monitoring the excitation spectra of the *naphthalene phosphorescence*, rather than the phosphorescence of the host crystal.

**4. Materials.** The ketones and aldehydes used in this investigation were purified either by recrystallization, or by column chromatography. Reagent grade solvents were used without further purification when they showed negligible emission at low temperatures.

## Results and Discussion

The S→T absorption spectra of a number of aromatic ketones and aldehydes have been measured by the phosphorescence excitation method, and these results are presented in Figures 2–18. The authenticity of the S→T absorption bands was considered established (i) when the 0–0 band in the absorption spectrum overlapped the 0–0 band in emission, (ii) when the phosphorescence spectrum did not change with wavelength of excitation in either the S→T or the S→S absorption regions, and, in the case of S→$T_{\pi,\pi}$ transitions, (iii) when an intermolecular heavy atom effect was observed. The first problem of interest was to determine the nature of the lowest triplet state and the nature and location of higher lying triplet states, where possible.

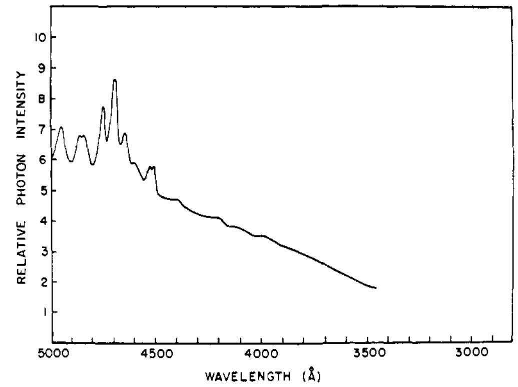

Figure 1. Spectral distribution of the photon intensity from a 450-w xenon lamp after passing through a Bausch and Lomb monochromator.

**A. Location of $T_{n,\pi}$ and $T_{\pi,\pi}$ States.** In order to distinguish between S→$T_{n,\pi}$ and S→$T_{\pi,\pi}$ transitions, the following criteria were used. The 0–0 band of the S→$T_{n,\pi}$ transition is usually located within about 2000 cm$^{-1}$ of the 0–0 band of the corresponding S→$S_{n,\pi}$ transition,[22] and should exhibit little or no enhancement upon addition of a heavy atom component to the solvent mixture.[23] Furthermore, when an n,π triplet state is the lowest triplet state of a molecule, the phosphorescence spectrum generally exhibits a prominent C=O vibrational progression and is short-lived (typically 10$^{-3}$ sec).[24] S→$T_{\pi,\pi}$ transitions, on the other hand, have no necessary location with respect to the 0–0 band of the S→$S_{n,\pi}$ transition, are very much weaker than S→$T_{n,\pi}$ transitions in the absence of a heavy atom effect, and should be intensified in a heavy atom solvent. When the emission occurs from a $T_{\pi,\pi}$ state, the vibrational structure of the phosphorescence spectrum is much different from that observed from a $T_{n,\pi}$ state, and lifetimes are usually considerably longer (on the order of a second in some cases).[15,25] When these various criteria were applied, most of the assignments could be made without difficulty.

The location and assignment of the lowest triplet state in a number of aromatic ketones and aldehydes are collected in Table I. In cases where it was possible to observe them, the assignment and location of higher triplet states are also given.

**1. Benzophenones. (a) Benzophenone.** The lowest triplet state of benzophenone was assigned as an n,π triplet state on the basis of the lifetime ($\sim 4 \times 10^3$ sec), singlet–triplet splitting (2200 cm$^{-1}$), and vibrational structure of the phosphorescence spectrum (1800-

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[23] M. A. El-Sayed, *J. Chem. Phys.*, **41**, 2462 (1964).

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[25] M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

Table I. Location of the Lowest n,π and π,π Triplet States and the n,π Singlet State[a]

| Compound | Obsd n,π* singlet state energy | Obsd n,π* triplet state energy | Obsd π,π* triplet state energy | Phosphorescence bands[b] |
|---|---|---|---|---|
| Benzophenone | 370<br>27.0 | 405<br>24.8 | . . . | 415 448<br>24.0 ← 1.8 → 22.2 |
| *p,p*'-Dibromobenzophenone | 380<br>26.4 | 415<br>24.1 | . . . | 420 452<br>23.8 ← 1.6 → 22.1 |
| *p,p*'-Dimethoxybenzophenone | 365<br>27.4 | 402<br>24.8 | . . . | 407 435<br>24.6 ← 1.6 → 23.0 |
| *p*-Hydroxybenzophenone | 375<br>26.5 | 413<br>24.2 | . . . | 423 450<br>23.8 ← 1.6 → 22.2 |
| Acetophenone | 360<br>27.8 | 378<br>26.5 | . . . | 385 412<br>26.0 ← 1.8 → 24.2 |
| 4'-Bromoacetophenone | 363<br>27.6 | 378<br>26.5 | 390<br>25.6 | 402 428<br>24.8 23.4 |
| 2,4'-Dibromoacetophenone | 375<br>26.6 | 390<br>25.6 | 403<br>24.3 | 413 438<br>24.2 22.8 |
| 4'-Hydroxyacetophenone | 346<br>28.9 | 361<br>27.8 | 395<br>25.3 | 400 418 432<br>25.0 24.0 23.2 |
| 4'-Methoxyacetophenone | 353<br>28.4 | 365<br>27.4 | 394<br>25.3 | 405 433<br>24.8 ← 1.6 → 23.2 |
| Butyrophenone | 365<br>27.4 | . . . | . . . | 398 424<br>25.1 ← 1.5 → 23.6 |
| *p*-Chlorobutyrophenone | 370<br>27.0 | 392<br>25.6 | . . . | 397 424<br>25.2 ← 1.6 → 23.6 |
| *p*-Methylbutyrophenone | 365<br>27.4 | 386<br>26.0 | . . . | 396 422<br>25.3 ← 1.5 → 23.8 |
| *p*-Acetamidobutyrophenone | 358<br>28.0 | . . . | 407<br>24.6 | 412 425 440<br>24.2 23.6 22.8 |
| *p*-Hydroxybutyrophenone | 345<br>29.0 | . . . | 399<br>25.1 | 410 428 440<br>24.4 23.4 22.8 |
| Benzaldehyde | 365<br>27.4 | 391<br>25.6 | . . . | 398 426<br>25.1 ← 1.5 → 23.6 |
| 4'-Bromobenzaldehyde | 370<br>27.0 | 398<br>25.1 |  | 410 438<br>24.4 ← 1.6 → 22.8 |
| 2-Naphthaldehyde | 350<br>28.6 | 382<br>26.2 | 478<br>20.9 | 490 525<br>20.4 ← 1.4 → 19.0 |

[a] Energies are given both in mμ and in units of 1000 cm$^{-1}$ (kK). [b] The positions of the 0–0 and the 0–1 bands in phosphorescence are given along with the spacing (in kK) between these two bands.

cm$^{-1}$ spacing between vibronic bands) (see Figure 2). There was no heavy atom solvent effect on the intensity of the S→T$_{n,\pi}$ transition. This assignment is, of course, in agreement with the previously proposed assignment.[24] The benzophenone results are useful in that they establish a set of characteristics which can be used to locate n,π triplet states in substituted benzophenones.

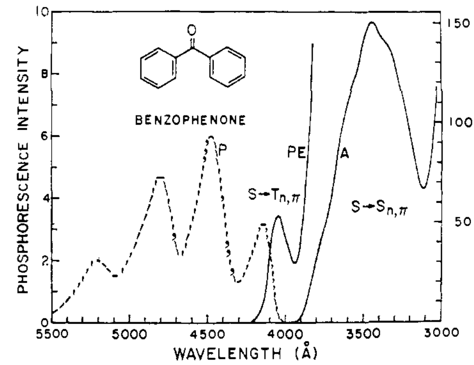

Figure 2. The absorption (A), phosphorescence excitation (PE), and phosphoresence (P) spectra of benzophenone. A was measured in toluene; P and PE were measured in EET.

(b) ***p,p*'-Dimethoxybenzophenone.** The lowest triplet state of *p,p*'-dimethoxybenzophenone was also assigned as an n,π state on the basis of the observed small singlet–triplet splitting (2500 cm$^{-1}$) and the regular 1600-cm$^{-1}$ spacing between vibronic bands in the phosphorescence spectrum (see Figure 3).

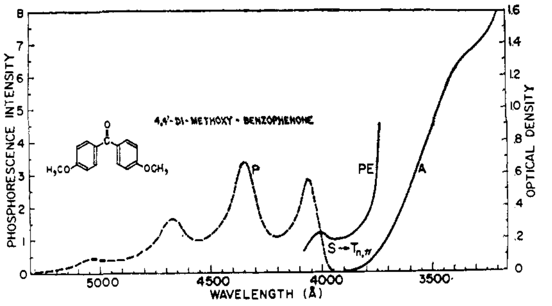

Figure 3. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of *p,p*'-dimethoxybenzophenone. A was measured in toluene; P and PE were measured in EET.

(c) ***p*-Hydroxybenzophenone.** Originally, the lowest triplet state of *p*-hydroxybenzophenone was assigned as a π,π triplet state,[26] but recently it was reassigned as an n,π triplet state.[27] With unpurified commercial material we did observe an emission spectrum which might be attributed to emission from a π,π triplet state, but, upon purification, this emission was not observed.

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(26) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).
(27) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965).

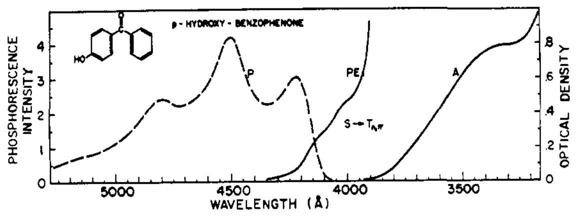

Figure 4. The absorption (A), phosphorescence excitation (PE), and phosphorescence (P) spectra of *p*-hydroxybenzophenone. A was measured in toluene; P and PE were measured in EET.

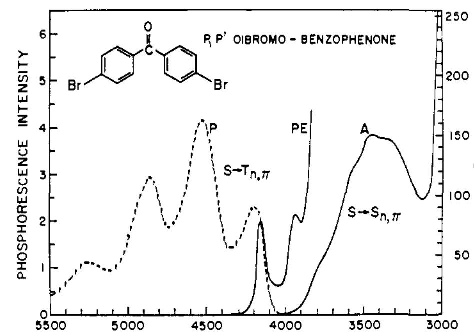

Figure 5a. The absorption (A), phosphoresence excitation (PE), and phosphorescence (P) spectra of *p,p'*-dibromobenzophenone. A was measured in toluene; P and PE were measured in EET.

With purified material we observed that the lifetime of the *p*-hydroxybenzophenone phosphorescence is shorter than that of benzophenone; the phosphorescence spectrum is clearly characteristic of emission from an $n,\pi$ triplet state (1600 $cm^{-1}$ vibrational progression) (see Figure 4); and the singlet–triplet splitting (2300 $cm^{-1}$) is that expected for an $n,\pi$ triplet state. There was no heavy atom effect on the intensity of the singlet–triplet transition. These observations definitely confirm the more recent assignment of the lowest triplet as an $n,\pi$ triplet state.

**(d) *p,p'*-Dibromobenzophenone.** The lowest triplet state of *p,p'*-dibromobenzophenone was assigned as an $n,\pi$ triplet state on the basis of the phosphorescence emission spectrum (prominent 1700-$cm^{-1}$ vibrational progression), lifetime (shorter than benzophenone), and position with respect to the 0–0 band of the $S \rightarrow S_{n,\pi}$ transition (singlet–triplet splitting ~2200 $cm^{-1}$).

In addition to the 0–0 band of the $S \rightarrow T_{n,\pi}$ transition which occurs at 24.1 kK, a second, higher energy absorption band was observed at 25.4 kK (see Figure 5a). Although we cannot at present rule out the possibility that this second band represents a transition to a $\pi,\pi$ triplet state, the following data suggest that this band should be assigned as the 0–1 of the $S \rightarrow T_{n,\pi}$ transition: (i) the splitting between this band and the 0–0 band of the $S \rightarrow T_{n,\pi}$ transition (1300 $cm^{-1}$) is very nearly the same as the splitting between the 0–0 and the 0–1 bands of the $S \rightarrow S_{n,\pi}$ transition; (ii) the polarizations of the 0–0 $S \rightarrow T_{n,\pi}$ band and the 25.4-kK band in a single crystal of *p,p'*-dibromobenzophenone were measured and both were found to have the same polarization (see Figure 5b); (iii) the 25.4-kK band is probably too strong for a $S \rightarrow T_{\pi,\pi}$ transition.

With benzophenone and the three derivatives which we investigated, it has not been possible to find evidence for a $S \rightarrow T_{\pi,\pi}$ transition at energies greater than the $S \rightarrow T_{n,\pi}$ transition. Since $S \rightarrow T_{\pi,\pi}$ transitions are predicted to be considerably weaker than $S \rightarrow T_{n,\pi}$ transitions, even in the presence of heavy atoms (see section C), this was not really an unexpected result. In benzophenone, for example, direct absorption measurements indicate that the extinction coefficient for the $S \rightarrow T_{n,\pi}$ transition is on the order of 0.04,[20] whereas the $S \rightarrow T_{\pi,\pi}$ transitions of aromatic hydrocarbons dissolved in a 30% solution of ethyl iodide typically are on the order of 0.01.[17]

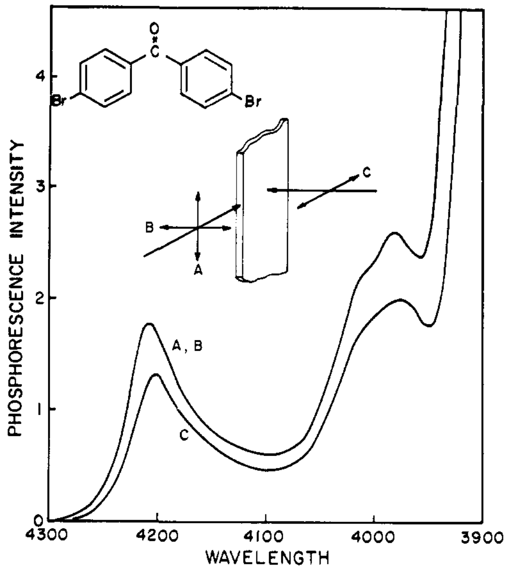

Figure 5b. The polarization of the phosphorescence excitation spectrum of a single crystal of *p,p'*-dibromobenzophenone: curve A, electric vector parallel to the needle axis; curve **B**, electric vector perpendicular to the needle axis and perpendicular to the cleavage plane; curve C, electric vector perpendicular to the needle axis and parallel to the cleavage plane.

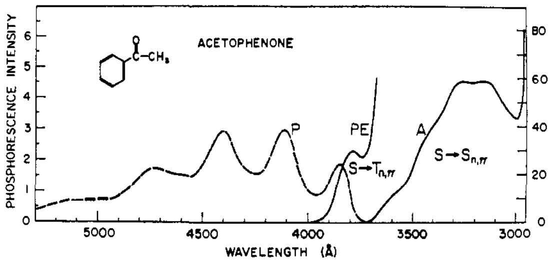

Figure 6. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of acetophenone. A was measured in toluene; P and PE were measured in EET.

**2. Acetophenones. (a) Acetophenone.** The singlet–triplet absorption spectrum of acetophenone is presented in Figure 6. A well-defined $S \rightarrow T$ absorption band was observed at 26.5 kK and assigned as a $S \rightarrow T_{n,\pi}$ transition on the basis of position with respect to the 0–0 band of the $S \rightarrow S_{n,\pi}$ transition (singlet–triplet splitting = 1300 $cm^{-1}$) and the vibrational structure of the phosphorescence spectrum (1800-$cm^{-1}$ vibrational progression).

**(b) 4'-Bromoacetophenone.** The phosphorescence excitation spectrum of 4'-bromoacetophenone (see Figure 7) exhibits a 0–0 band at 25.6 kK which we have assigned as a transition to the $\pi,\pi$ triplet state. This assignment was based on (i) the observation that the $S \rightarrow S_{n,\pi}$ transitions in both acetophenone and 4'-

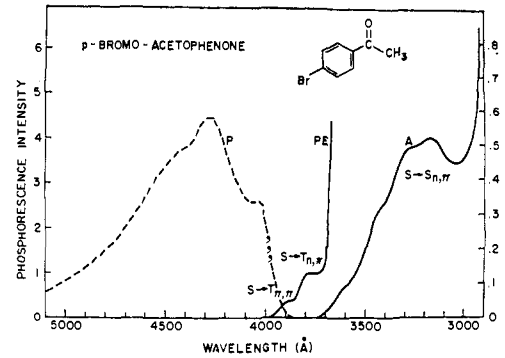

Figure 7. The absorption (A), phosphoresence excitation (PE), and phosphorescence (P) spectra of 4′-bromoacetophenone. A and P were measured in EET, whereas PE was obtained using a crystalline sample doped with naphthalene.

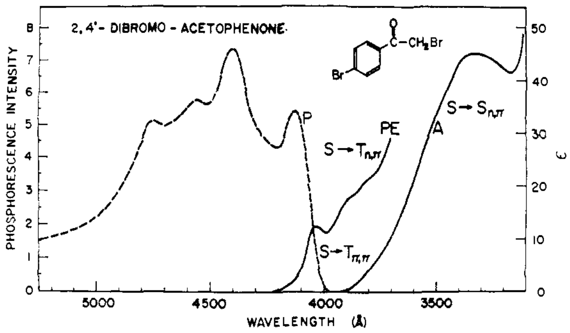

Figure 8. The absorption (A), phosphorescence excitation (PE), and phosphorescence (P) spectra of 2,4′-dibromoacetophenone. A and P were measured in EET, whereas PE was obtained using a crystalline sample doped with naphthalene.

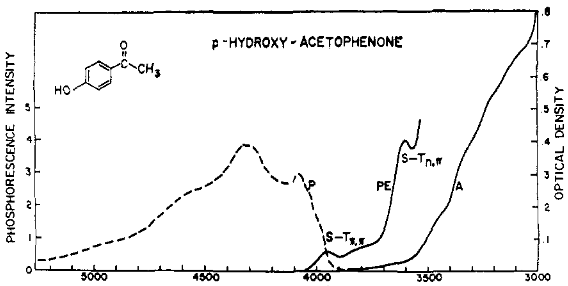

Figure 9. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of 4′-hydroxyacetophenone. A was measured in toluene; P and PE were measured in TEEE.

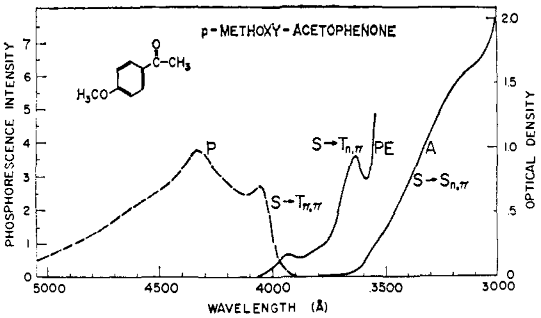

Figure 10. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of 4′-methoxyacetophenone. A was measured in benzene; P and PE were measured in TEEE.

bromoacetophenone occur at about the same energy, whereas the phosphorescence emission from the 4′-bromoacetophenone is red shifted some 1200 cm$^{-1}$ from that of acetophenone, and (ii) the fact that the phosphorescence spectrum of 4′-bromoacetophenone does not exhibit a vibrational progression characteristic of the C=O stretching frequency. No external heavy atom effect on the intensity of the S→T$_{\pi,\pi}$ transition was observed, presumably because of the larger internal heavy atom effect.

In the S→T absorption spectrum, a second more intense band was observed at 26.5 kK. We have assigned this as the 0–0 band of an S→T$_{n,\pi}$ transition because it is more intense than the lower energy π→π transition and because it has the proper location with respect to the S$_{n,\pi}$ state (the singlet–triplet splitting for the 26.5-kK transition is 1100 cm$^{-1}$, and this is very nearly the same as the splitting observed for the unsubstituted acetophenone).

(c) **2,4′-Dibromoacetophenone.** The phosphorescence excitation spectrum of 2,4′-dibromoacetophenone is presented in Figure 8. The 0–0 band is observed at 24.8 kK and a second, poorly resolved band is observed at 25.6 kK. The 24.8-kK band was assigned as a S→T$_{\pi,\pi}$ transition because of its location with respect to the 0–0 band of the S→S$_{n,\pi}$ absorption (the singlet–triplet splitting in this case is 1800 cm$^{-1}$, whereas the S$_{n,\pi}$–T$_{n,\pi}$ splitting observed in acetophenone was only 1300 cm$^{-1}$), and because the phosphorescence emission did not exhibit vibrational structure characteristic of emission from an n,π triplet state. The shoulder observed at 25.6 kK probably is a transition to the lowest n,π triplet state since the intensity of this transition is expected to be greater than the S→T$_{\pi,\pi}$ transition and since the position of the shoulder with respect to the 0–0 band of the S→S$_{n,\pi}$ transition is appropriate for an n,π triplet state, (singlet–triplet state splitting of about 1000 cm$^{-1}$).

(d) **4′-Hydroxyacetophenone.** The lowest singlet → triplet absorption band of 4′-hydroxyacetophenone was observed at 25.3 kK and assigned as a π,π triplet state for the following reasons: (i) the lifetime of the phosphorescence was long (~1 sec); (ii) the vibrational structure of the phosphorescence emission spectrum was irregular (a 1000-cm$^{-1}$ vibration spacing was observed); (iii) there is a large displacement of this band with respect to the S→S$_{n,\pi}$ absorption (about 3600 cm$^{-1}$); and (iv) this absorption band was enhanced by the heavy atom solvent (see Figure 9). A second, well-resolved singlet–triplet absorption band was observed at 27.8 kK and assigned as a transition to an n,π triplet state, since it was easily observed in the absence of a heavy atom solvent and, since it has the proper S$_{n,\pi}$–T$_{n,\pi}$ splitting (1100 cm$^{-1}$) for an acetophenone derivative.

(e) **4′-Methoxyacetophenone.** The phosphorescence excitation and phosphorescence spectra of 4′-methoxyacetophenone (see Figure 10) were found to be very similar to those observed with 4′-hydroxyacetophenone. The 0–0 band of the phosphorescence excitation spectrum was observed at 25.3 kK and assigned as a transition to a π,π triplet state. A more intense, well-defined higher energy band was observed at 27.4 kK and assigned as a transition to the n,π triplet state.

In all of the substituted acetophenones which we investigated, the ordering of the π,π and n,π triplet states was inverted from that found in acetophenone.

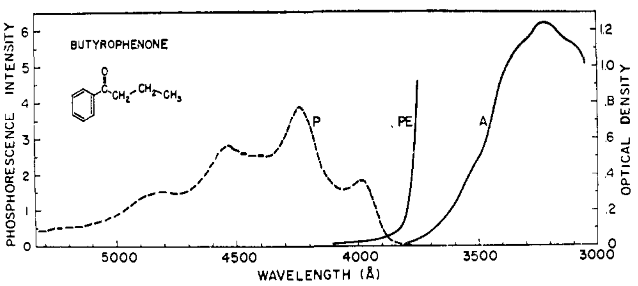

Figure 11. The absorption (A) and phosphoresence (P) spectra of butyrophenone. A was measured in toluene, P in EET.

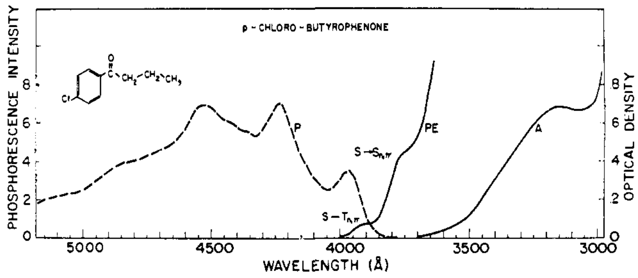

Figure 12. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of *p*-chlorobutyrophenone. A was measured in toluene; P and PE were measured in TEEE.

This sensitivity of the ordering of the n,π and π,π triplet states of acetophenone to alteration by substituents is perhaps reasonable in view of the fact that acetophenone has the highest energy n,π triplet state of all of the unsubstituted aldehydes and ketones which we studied. It is generally observed that substituents such as bromo, methoxy, and hydroxy red shift π→π transitions much more than they shift n→π transitions.[28] Therefore, acetophenone with its relative higher energy n,π triplet state is expected to be more susceptible to substituent effects on the ordering of the n,π and π,π triplet states and the other ketones and aldehydes.

Yang has investigated the photochemical and phosphorescence properties of methyl-substituted acetophenones and arrived at very similar conclusions regarding substituent effects on the ordering of n,π and π,π triplet states in acetophenone.[29]

**3. Butyrophenones. (a) Butyrophenone.** Butyrophenone did not exhibit a well-resolved singlet–triplet absorption spectrum, but for comparison with other substituted butyrophenones, its $S \rightarrow S_{n,\pi}$ absorption and phosphorescence emission spectra (lifetime = $2 \times 10^{-3}$ sec[30]) are presented in Figure 11. The phosphorescence emission is clearly identifiable as emission from an n,π triplet state.

(b) ***p*-Chlorobutyrophenone.** As shown in Figure 12, *p*-chlorobutyrophenone exhibits a phosphorescence excitation spectrum with a 0–0 band at 25.6 kK. Because of the close similarity between the phosphorescence spectra and $S \rightarrow S_{n,\pi}$ absorption spectra of butyrophenone and *p*-chlorobutyrophenone, it would appear that the lowest triplet state of *p*-chlorobutyrophenone should also be assigned as a transition to an n,π triplet state. The phosphorescence excitation spectrum of *p*-chlorobutyrophenone is somewhat puzzling in that a heavy atom solvent was required in order to observe S→T transition. Since there is generally no external heavy atom effect on $S \rightarrow T_{n,\pi}$ transitions, the triplet-state assignment in this case is not as certain as the other ones.

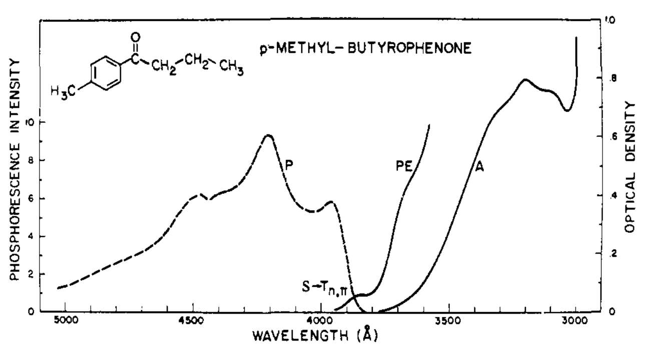

Figure 13. The absorption (A), phosphoresence excitation (PE), and phosphorescence (P) spectra of *p*-methylbutyrophenone. A was measured in toluene; P and PE were measured in TEEE.

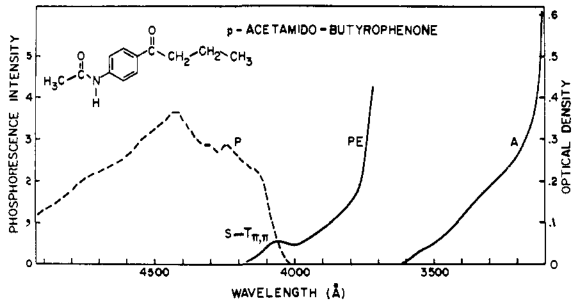

Figure 14. The absorption (A), phosphoresence excitation (PE), and phosphorescence (P) spectra of *p*-acetamidobutyrophenone. A was measured in toluene; P and PE were measured in TEEE.

(c) ***p*-Methylbutyrophenone.** The 0–0 band of the phosphorescence excitation spectrum of *p*-methylbutyrophenone was observed at 26.0 kK (see Figure 13). On the basis of the position of this band with respect to the 0–0 band of the $S \rightarrow S_{n,\pi}$ transition, the nature of the phosphorescence emission spectrum (vibrational spacing of 1400 $\text{cm}^{-1}$) and the close similarity between the $S \rightarrow S_{n,\pi}$ spectra of butyrophenone and *p*-methyl- and *p*-chlorobutyrophenone, this band was assigned as a transition to an n,π triplet state. However, again, as with *p*-chlorobutyrophenone, a heavy atom solvent was required in order to observe the $S \rightarrow T_{n,\pi}$ transition.

(d) ***p*-Acetamidobutyrophenone.** The lowest singlet–triplet absorption band in *p*-acetamidobutyrophenone was observed at 24.6 kK (see Figure 14). This band was assigned as a transition to a π,π triplet state because: (i) it is displaced over 3400 $\text{cm}^{-1}$ from the 0–0 band of the $S \rightarrow S_{n,\pi}$ transition; (ii) the phosphorescence lifetime was long (0.06 sec[30]); (iii) the shape of the phosphorescence emission spectrum was not characteristic of emission from an n,π triplet state (600-$\text{cm}^{-1}$ vibrational spacing); and (iv) the S→T absorption was enhanced by the heavy atom solvent.

(e) ***p*-Hydroxybutyrophenone.** A singlet–triplet absorption band was observed with *p*-hydroxybutyrophenone at 25.1 kK (see Figure 15). In view of the considerable displacement (3500 $\text{cm}^{-1}$) of this transition

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(28) J. Petruska, *J. Chem. Phys.*, **34**, 1120 (1961).

(29) N. C. Yang, private communication.

(30) E. J. Baum, J. K. S. Wan, and J. N. Pitts, *J. Am. Chem. Soc.*, **88**, 2652 (1966).

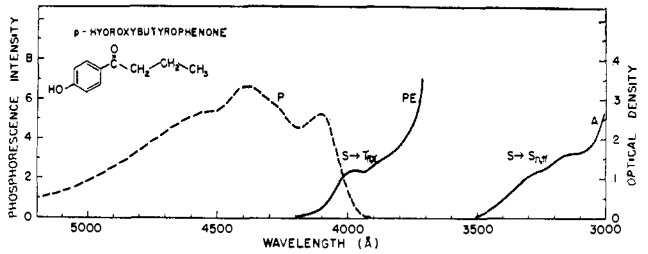

Figure 15. The absorption (A), phosphorescence excitation (PE), and phosphorescence (P) spectra of $p$-hydroxybutyrophenone. A was measured in toluene; P and PE were measured in TEEE.

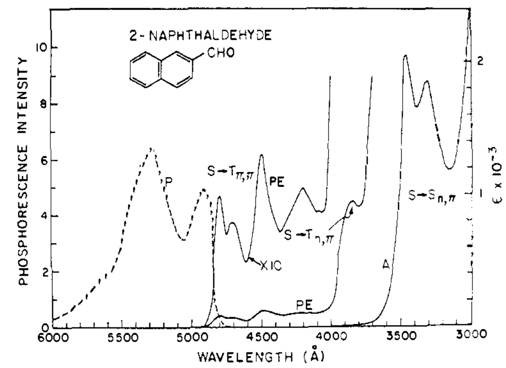

Figure 16. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of 2-naphthaldehyde. A was measured in toluene; P and PE were measured in TEEE.

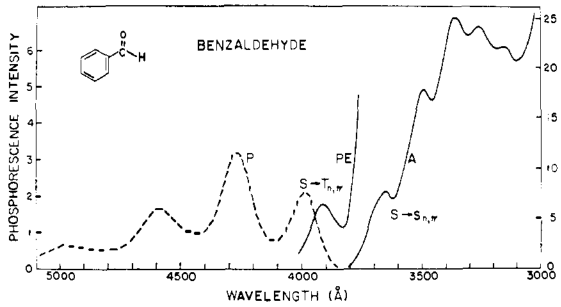

Figure 17. The absorption (A), phosphorescence excitation (PE), and phosphorescence (P) spectra of benzaldehyde. A was measured in toluene; P and PE were measured in EET.

from the S→$S_{n,\pi}$ transition, the phosphorescence lifetime (0.08 sec[30]), and shape of the phosphorescence emission spectrum (vibrational spacing 1000 cm$^{-1}$), the 25.1-kK band was assigned as a transition to a $\pi,\pi$ triplet state.

**4. Aldehydes.** 2-Naphthaldehyde, benzaldehyde, and 4′-bromobenzaldehyde all exhibited well-resolved S→$T_{n,\pi}$ absorption bands at very nearly the same energy (26.2, 25.6, and 25.1 kK, respectively), as might have been anticipated from the similarity in the location of the 0–0 band of the S→$S_{n,\pi}$ transition in these molecules (28.6, 27.4, and 27.0 kK, respectively). The spectra for these compounds are presented in Figures 16–18. In addition to a S→$T_{n,\pi}$ transition at 26.2 kK, 2-naphthaldehyde also exhibits a well-defined naphthalene-like singlet–triplet absorption spectrum at lower energies, with an origin at 20.9 kK.

A summary of the assignments and locations of the lower triplet states of the aromatic ketones which we

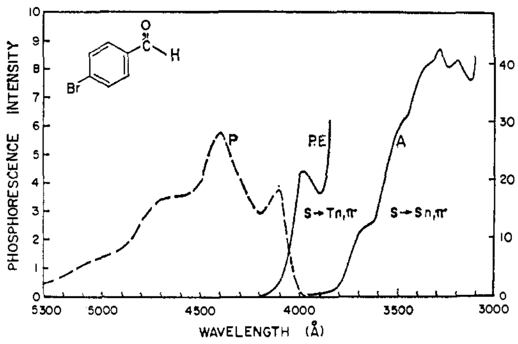

Figure 18. The absorption (A), phosphoresence excitation (PE), and phosphoresence (P) spectra of 4′-bromobenzaldehyde. A was measured in toluene; P and PE were measured in EET.

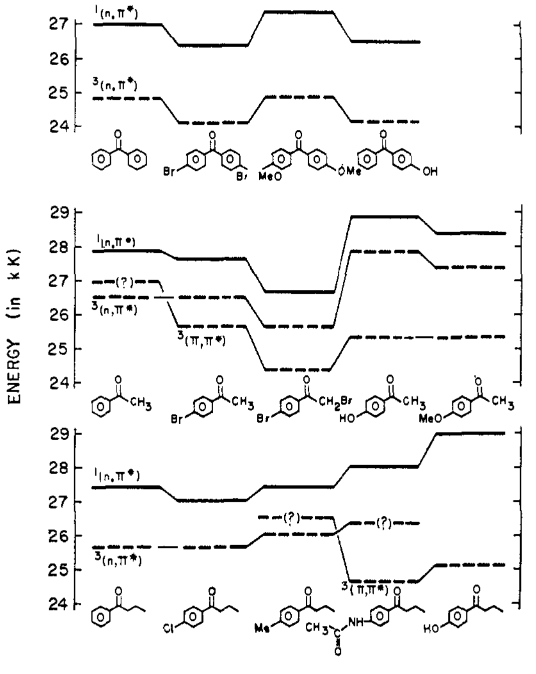

Figure 19. Energy of the lowest singlet (n,π) and the lower triplet states of aromatic ketones.

have studied is presented in Figure 19, along with the location of the lowest singlet n,π states.

With these data on the ketone and aldehyde singlet–triplet absorption spectra, we now turn to a consideration of some of the current notions regarding intersystem-crossing rates in carbonyl compounds and, in particular, the role which $\pi,\pi$ triplet states are presumed to play in this process.

**B. Location of the $T_{\pi,\pi}$ States and Relation to the Theory of Intersystem Crossing in Carbonyl Compounds.** It has been known for some time that the efficiency of intersystem crossing in aromatic carbonyl compounds such as benzophenone and acetophenone is high.[25] Recently Lamola and Hammond,[31] using triplet-state sensitized chemical reactions as triplet-state counters, and Borkman and Kearns,[20] using the phosphorescence excitation method, have demonstrated that the quantum yield for intersystem crossing in these two molecules is ~1.00.

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(31) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

On the basis of a consideration of spin–orbit coupling, it has been proposed that intersystem crossing is very rapid ($10^{10}$ sec$^{-1}$) in heteroaromatic molecules when it occurs between a $S_{n,\pi}$ state and a lower lying $T_{\pi,\pi}$ state.[14,15] When intersystem crossing occurs directly from a $S_{n,\pi}$ to a $T_{n,\pi}$ state, the rate is predicted to be much slower (on the order of $10^7$ sec$^{-1}$). Consequently, in order to account for the fact that benzophenone and acetophenone are nonfluorescent, it is suggested[15] that in these molecules (and presumably in many other aromatic ketones) a $T_{\pi,\pi}$ state lies interposed between the lowest n,π singlet state and the lower lying n,π triplet state. We were naturally interested to see whether or not spectroscopic evidence could be found for these intervening $T_{\pi,\pi}$ states in the aromatic ketones which we investigated. We found no evidence for such a state in any of the benzophenones or the butyrophenones, but this probably can be attributed to the weakness of $S \rightarrow T_{\pi,\pi}$ transitions relative to $S \rightarrow T_{n,\pi}$ transitions (see section C).

In the substituted acetophenones which we studied, the ordering of the lower triplet states was inverted from that found in acetophenone; the $T_{\pi,\pi}$ state in each case was found to lie below the $T_{n,\pi}$ state. Because of the close proximity of the $T_{n,\pi}$ and $T_{\pi,\pi}$ states in several of the substituted acetophenones (the bromo derivative, in particular), it seems fairly safe to conclude that *the* $T_{\pi,\pi}$ *state in acetophenone lies just above the lowest* $T_{n,\pi}$ *state, but still below the* $S_{n,\pi}$ *state.* Our singlet → triplet absorption spectra, therefore, tend to support the theoretical proposal that the lowest $T_{\pi,\pi}$ state in acetophenone (and probably in benzophenone and in a number of other aromatic ketones) lies sandwiched between the lowest $S_{n,\pi}$ and the $T_{n,\pi}$ states. Higher resolution and lower temperature measurements will be required to locate the $T_{\pi,\pi}$ states in those ketones where the $T_{n,\pi}$ state is the lowest triplet state.

**C. External Heavy Atom Effects on the Intensity of $S \rightarrow T_{n,\pi}$ and $S \rightarrow T_{\pi,\pi}$ Transitions.** A point of further interest in connection with our investigation of the S→T absorption spectra of aromatic carbonyl compounds was the effect which external heavy atoms exert on the intensity of the $S \rightarrow T_{n,\pi}$ and $S \rightarrow T_{\pi,\pi}$ transitions.

El-Sayed has examined spin–orbit coupling effects in carbonyl compounds and predicted that there should be no intramolecular heavy atom effect on the intensity of $S \rightarrow T_{n,\pi}$ transitions.[14,23] He further noted that, at least with the aromatic hydrocarbons, intermolecular heavy atom effects are always much smaller than intermolecular heavy atom effects, and concluded on this basis that there should be no intermolecular heavy atom effect on the intensity of the $S \rightarrow T_{n,\pi}$ transitions. That external heavy atom effects should necessarily be smaller than internal heavy atom effects on the $S \rightarrow T_{n,\pi}$ transitions of carbonyl compounds seems to be a questionable assumption. Nevertheless, it is possible to check the suggestion that $S \rightarrow T_{n,\pi}$ transitions should not be enhanced by an external heavy atom effect.

The intensification of $S \rightarrow T_{\pi,\pi}$ transitions in aromatic hydrocarbons by heavy atom solvents has been the subject of many previous investigations.[17,18,32,33] The oscillator strength of the lowest $S \rightarrow T_{\pi,\pi}$ transition of naphthalene, for example, is enhanced by $\Delta f \simeq 6 \times 10^{-8}$ when dissolved in ethyl iodide. Since our heavy atom solvents contained only 30% ethyl iodide, we could expect the oscillator strength for a $S \rightarrow T_{\pi,\pi}$ transition in an aromatic carbonyl compound to be increased by roughly $\Delta f = 2 \times 10^{-8}$. In view of the expected intensity of $S \rightarrow T_{\pi,\pi}$ transitions in carbonyl compounds in the absence of any heavy atom effect (see section D), these very rough estimates suggest that $S \rightarrow T_{\pi,\pi}$ transition in aromatic carbonyl compounds should be enhanced by perhaps a factor of 2 upon addition of 30% ethyl iodide to the solvent.

Experimentally the effect of a heavy atom solvent on the intensity of both the $S \rightarrow T_{n,\pi}$ and the $S \rightarrow T_{\pi,\pi}$ transitions was examined by comparing the intensity of the phosphorescence excitation spectra of samples dissolved in the heavy atom solvent and in the nonheavy atom solvent. This actually provides a fairly sensitive test of heavy atom solvent effects on the intensity of S→T transitions because the intensity of the phosphorescence is proportional, among other things, to both the extinction coefficient, $\epsilon$, for the singlet–triplet transition and the probability, $X$, that a triplet-state molecule will return radiatively to its ground state. For those cases where $X$ is less than unity (the usual situation), an enhancement in $\epsilon$ will usually lead to an enhancement in $X$ too.

The results of an investigation of heavy atom effects on the intensity of $S \rightarrow T_{n,\pi}$ transitions in a number of molecules are presented in Table II. In accordance with the theoretical predictions of El-Sayed, we find that in those molecules where the lowest triplet state is definitely assigned as a $T_{n,\pi}$ state, there is no external heavy atom effect on the intensity of S→T transitions.[34] In those molecules where the lowest triplet state is a $T_{\pi,\pi}$ state, we observed an enhancement of both the $S \rightarrow T_{\pi,\pi}$ and $S \rightarrow T_{n,\pi}$ transitions. The enhancement of the $S \rightarrow T_{\pi,\pi}$ transition is clearly due to an enhancement of both $\epsilon$ and $X$. In view of our findings with other molecules, we can attribute the *apparent* enhancement of the $S \rightarrow T_{n,\pi}$ transitions in those molecules which have a *lower* lying $T_{\pi,\pi}$ state to an enhancement of $X$. Proceeding on this assumption we have normalized the singlet–triplet absorption spectra for the *p*-hydroxy- and *p*-methoxyacetophenones such that $S \rightarrow T_{n,\pi}$ transitions have the same intensity in the two different solvent systems (see Figure 20). This is

**Table II.** The Effect of Heavy Atom Solvents on the Intensity of $S \rightarrow T_{n,\pi}$ Transitions

| Compound | $I_{\text{phos}}$ (in TEEE)/ $I_{\text{phos}}$ (in EET) |
|---|---|
| Benzaldehyde | 1.0 (± 10%) |
| Benzophenone | 1.1 |
| *p*-Hydroxybenzophenone | 1.0 |
| 4,4′-Dibromobenzophenone | 1.0 |
| Acetophenone | 1.0 |

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(32) S. P. McGlynn, R. Sunseri, and N. Christodoyleas, *J. Chem. Phys.*, **37**, 1818 (1962).

(33) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. O. Christodoyleas, *J. Phys. Chem.*, 66, 2499 (1962).

(34) In a preliminary account of this work (ref 21) we originally reported that $S \rightarrow T_{n,\pi}$ transitions were apparently enhanced by the addition of a heavy atom component to the solvent. Subsequent investigations demonstrated, however, that this apparent enhancement could be attributed to cracking of the glassing mixture. When care was taken to ensure that the glasses were not cracked, we observed no enhancement of the intensity of the $S \rightarrow T_{n,\pi}$ transition upon addition of a heavy component to the solvent mixture.

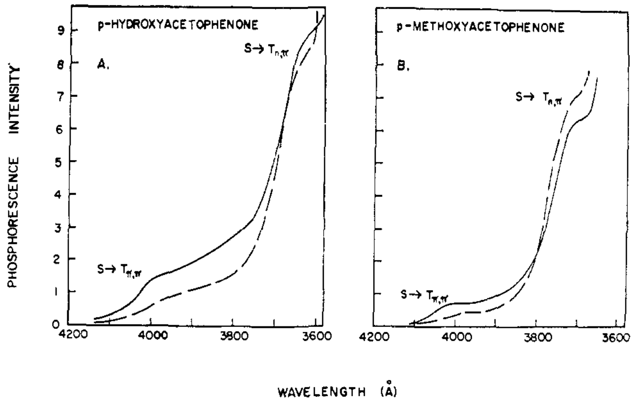

Figure 20. Illustration of the effect of ethyl iodide on the intensity of the phosphoresence excitation spectra of *p*-hydroxyacetophenone (A) and *p*-methoxyacetophenone (B). The dashed curves were obtained using ether, toluene, and ethanol (EET) as the solvent, whereas the solid curves were obtained using toluene, ether, ethanol, and ethyl iodide (TEEE) as the solvent. The curves have been normalized so that the intensity of the $S \rightarrow T_{n,\pi}$ transition is approximately the same in the two different solvents. This normalization procedure approximately corrects the phosphorescence excitation spectra for the heavy atom effect on $X$ (see text).

equivalent to removing the effect of the heavy atom on $X$ and leaves only the heavy atom effect on $\epsilon$. From the spectra presented in Figure 20 we further note that the addition of a heavy atom component to the solvent increases the intensity of the $S \rightarrow T_{\pi,\pi}$ transitions by about a factor of 2, in accord with our theoretical predictions.

It would appear from these results, and the results of an investigation of heavy atom effects on the n,$\pi$ triplet state of benzophenone,[20] that the effect of heavy atom solvents can be used to determine the assignment of the lowest triplet state of an aromatic carbonyl compound. If there is no heavy atom effect on the phosphorescence excitation spectrum, or on the triplet-state lifetime of a nonheavy atom containing aromatic carbonyl compounds, this can be taken as conclusive evidence that the lowest triplet state is an n,$\pi$ triplet state. If it were not for the data on the *p*-methyl- and *p*-chlorobutyrophenones, we would be tempted to suggest that the observation of a heavy atom effect on the intensity of the phosphorescence excitation spectrum could be taken as evidence that the lowest triplet state of a molecule is a $\pi,\pi$ triplet state. Although we tentatively assigned the lowest triplet state of these two molecules as $T_{n,\pi}$ states, a heavy atom effect on the intensity of the $S \rightarrow T$ spectrum was observed. It is these latter results which make it difficult to make a more general statement regarding the heavy atom effect on $S \rightarrow T_{n,\pi}$ absorption spectra.

**D. Intensification of $S \rightarrow T_{\pi,\pi}$ Transitions by the Carbonyl Group.** In addition to locating triplet states, our $S \rightarrow T$ absorption spectra also provide information regarding the intensity of $S \rightarrow T_{\pi,\pi}$ transitions relative to the $S \rightarrow T_{n,\pi}$ transitions.

Theoretically we find that the $S \rightarrow T_{\pi,\pi}$ transitions in aromatic carbonyl compounds should be considerably more intense than in the parent aromatic hydrocarbon. This intensification of the $S \rightarrow T_{\pi,\pi}$ transitions occurs in the following way. Consider, for simplicity, formaldehyde. Sidman has previously shown that the spin-orbit perturbation in this molecule mixes the lowest triplet $n_2,\pi_2$ state ($^3A_2$) with a high-lying singlet $\pi_1,\pi_2$ state ($^1A_1$) through $\sigma_z$, the $z$ component of the spin-orbit perturbation.[8] This mixing gives rise to the following one-electron integral

$$\left(\frac{e\hbar^2}{(2mc)^2}\right)^2[\langle n(i)|\sigma_z(i)|\pi_1(i)\rangle]^2$$

which Sidman calculated to have a value of $2.2 \times 10^{-5}$ (ev)$^2$.[8] This same integral occurs in the mixing of the $\pi_1,\pi_2$ triplet state with the corresponding n,$\pi_2$ singlet state. Now it is known that spin-orbit interaction between $\pi_1,\pi_2$ singlet and triplet states is negligible in both the parent hydrocarbon and in the aromatic carbonyl compound because of the vanishing of one- and two-center terms.[11] We therefore predict that mixing between the $\pi_1,\pi_2$ triplet state and an n,$\pi_2$ singlet state in the carbonyl compound will lead to a considerable intensification of the $S \rightarrow T_{\pi_1,\pi_2}$ transition over that which would be observed if there were no mixing between $T_{\pi_1,\pi_2}$ and $S_{n,\pi_2}$ states. To obtain an estimate of the intensity expected for a $S \rightarrow T_{\pi_1,\pi_2}$ transition in a carbonyl compound, we make use of the data on formaldehyde.

In formaldehyde the oscillator strength for the $S \rightarrow S_{n,\pi_2}$ transition is on the order of $2.4 \times 10^{-4}$.[10] The location of the $\pi_1,\pi_2$ triplet state in this molecule is unknown, but it probably lies within 2 ev of the lowest n,$\pi_2$ singlet state. The oscillator strength for the $S \rightarrow T_{\pi_1,\pi_2}$ transition is therefore predicted to be on the order of $2.4 \times 10^{-4} \times (2.2 \times 10^{-5}\ \text{ev}^2)/(2)^2\ \text{ev}^2 \simeq 0.13 \times 10^{-8}$. In the aromatic ketones where the $S_{n,\pi}$ and $T_{\pi,\pi}$ states are less than 0.5 ev apart, the intensity of the $S \rightarrow T_{\pi,\pi}$ transition could be on the order of $2 \times 10^{-8}$. For comparison, we note that Sidman predicted that the intensity of the $S \rightarrow T_{n,\pi_2}$ transition to be on the order of $1.5 \times 10^{-7}$.[10] We therefore expect the $S \rightarrow T_{n,\pi_2}$ transition to be about 10 to 100 times more intense than the $S \rightarrow T_{\pi_1,\pi_2}$ transition. This probably accounts for the fact that we were unable to observe transitions to $T_{\pi,\pi}$ states when an $S \rightarrow T_{n,\pi}$ transition occurred at lower energies.

Certainly these results apply strictly only to formaldehyde, but similar results can be expected with aromatic carbonyl compounds. The fact that the oscillator strengths for the $S \rightarrow T_{n,\pi}$ transitions in benzaldehyde ($1.8 \times 10^{-7}$), acetophenone ($1.3 \times 10^{-7}$), and benzophenone ($3 \times 10^{-7}$)[35] are, within a factor of 2 to 3, equal to that estimated for formaldehyde provides some experimental support for this expectation.

Experimentally we do find evidence for the predicted enhancement of the $S \rightarrow T_{\pi,\pi}$ transition in several of the carbonyl compounds which we studied. These data are presented in Figure 20 for *p*-hydroxy- and *p*-methoxyacetophenone. In these two compounds the lowest triplet state is a $\pi,\pi$ triplet state, and the transition to this state could be observed *without use of a heavy atom solvent.* Under these conditions, the extinction coefficients for the $S \rightarrow T_{\pi,\pi}$ transitions were about 10-fold smaller than for the $S \rightarrow T_{n,\pi}$ transitions, in reasonable agreement with our rough theoretical estimates. It should be pointed out that under *comparable* experimental conditions, it has not been possible to observe the $S \rightarrow T_{\pi,\pi}$ transitions of the parent aromatic hydro-

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(35) Y. Kanda, H. Kaseda, and T. Matmura, *Spectrochim. Acta*, 20, 1387 (1964).

carbons without the use of a heavy atom solvent system.[36,37]

**E. Relation of the Spectroscopic Results to Ketone Photochemistry.** One of the most thoroughly studied photochemical reactions of the carbonyl compounds is the photoreduction in the presence of good hydrogen atom donors.[38–41] From studies of a number of aromatic ketones it appears that the reactive species is an n,$\pi$ triplet state.[38–41] In those ketones where the lowest triplet state is a $\pi,\pi$ triplet state, the molecules are considerably less reactive, or totally unreactive. Our triplet-state assignments in the benzophenone series are therefore consistent with the observations that the 4,4′-dimethyl-, -dimethoxy-, and -dibromobenzophenone all readily photopinacolize.[38] The "anomalous" nonreactivity of *p*-hydroxybenzophenone has been previously considered by Porter[27] in terms of the excited state p*K*. Many of the butyrophenones are known to undergo a photochemical reaction which is analogous to the type II cleavage of ketones, and again reactivity can generally be correlated with relative ordering of the n,$\pi$ and $\pi,\pi$ triplet states.[42] In both 4′-chloro- and 4′-methylbutyrophenone the lowest triplet state has been assigned as an n,$\pi$ triplet state, and both compounds show a high quantum yield for the type II process.[43] In *p*-hydroxy- and *p*-acetamidobutyrophenone, on the other hand, the lowest triplet state is a $\pi,\pi$ triplet state, and these molecules do not undergo a type II photochemical reaction.[30] Similarly, the nonreactivity of 2-naphthaldehyde has already been attributed to the fact that the lowest triplet state is a $\pi,\pi$ triplet state.[44]

As we pointed out in section A, all of the acetophenone derivatives which we studied, including 4′-acetamido-, 4′-bromo-, 4′-hydroxy-, 4′-methoxy-, and 2,4′-dibromoacetophenone, have a $\pi,\pi$ triplet state as their lowest triplet state. Therefore, to the extent that the correlation between reactivity and location of the n,$\pi$ triplet state is valid, these substituted acetophenones should be photochemically less reactive than acetophenone.

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(36) $S \rightarrow T_{\pi,\pi}$ transitions have also been observed in a number of coumarin derivatives without the use of heavy atom solvents: W. Rothman and D. R. Kearns, presented at the Western Regional Meeting the American Chemical Society, Los Angeles, Calif., Nov 1965.

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# Free-Radical Addition of Trifluoroacetonitrile to Ethylene.
# III. Temperature Dependence and Reaction Energetics[1,2]

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**Abstract:** A study is reported of the rate of the gas-phase addition of $CF_3CN$ to ethylene over the range 365–445°. Under conditions such that $CF_3CN >> C_2H_4$, the rate equation is $(\partial/\partial t)[CF_3CH_2CH_2CN] = 10^{7.0\pm0.4} \exp(-27 \pm 3/RT)[CF_3CN][C_2H_4]$ mole l.$^{-1}$ sec$^{-1}$. Examination of this result relative to the over-all reaction energetics shows the initiation process to be bimolecular, $CF_3CN + C_2H_4 \longrightarrow CNCH_2CH_2 + CF_3$, and the kinetic chain length for the propagation cycle about 200 at 440°.

The telomerization of $CF_3I$ with ethylene has been investigated in the homogeneous gas phase (309°) by Bell.[4] A similar study, but with $CF_3CN$ and $C_2H_4$ at a higher temperature (442°), was reported by Gac and Janz.[5] Both centered on the propagation steps of these free-radical processes. The present communication reports the results of a study of the $CF_3CN$–$C_2H_4$ addition reaction over a temperature range from 365 to 445°. The results are examined for their significance relative to the reaction energetics of such gas-phase telomerizations and the mode of initiation of the free-radical mechanism.

## Kinetics

The reactants, $CF_3CN$ (Peninsular Chemresearch, Inc., 99% minimum) and $C_2H_4$ (Matheson Co., Inc., 99% minimum), were degassed under high vacuum and triply distilled at low temperatures prior to use.

The apparatus and procedure have been described in detail elsewhere.[5] Kinetic data were obtained by manometric techniques. Total initial reactant pressures were between 450 and 700 mm. The initial mole ratio of nitrile to olefin was maintained constant at 8.7:1.0. Analyses of both liquid and gaseous products

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(1) Based in part on a thesis submitted by J. B. F. in partial fulfillment of the requirements for the Ph.D. degree, Oct 1965, Rensselaer Polytechnic Institute, Troy, N. Y.

(2) Presented at the 152th National Meeting of the American Chemical Society, Division of Physical Chemistry, New York, N. Y., Sept 1966.

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