Electronic Transitions of Aromatic Carbonyl Compounds.

Sam Stewart Mims

Louisiana State University and Agricultural & Mechanical College

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ELECTRONIC TRANSITIONS OF AROMATIC CARBONYL COMPOUNDS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Sam Stewart Mims
B. S., Louisiana State University, 1952
May, 1958
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ABSTRACT

The lowest energy band in the absorption spectra of many aromatic carbonyl compounds results from a transition involving a non-bonding electron localized on the carbonyl oxygen. In these compounds the main process following absorption is the conversion of excited molecules to the lowest triplet state. Under suitable experimental conditions emission of light from this state can be easily observed.

Both of these processes, the lowest energy absorption and the emission, result from transitions localized largely in the carbonyl group. The present investigation records and interprets the effects of variations in molecular structure and the effects of various solvents on these transitions.

The position of the lowest energy absorption band is found to be determined largely by the electron density on the carbonyl carbon atom. Since the absorption process results in a transfer of negative charge away from the carbonyl oxygen toward the carbonyl carbon, a negative charge on this carbon atom opposes the transition. Therefore substituents on this atom or in the phenyl group attached to this atom
which are electron releasing shift this absorption to higher energy. Electron withdrawing groups shift the absorption to lower energy.

Doubling of the vibrational structure is found both in the n-pi absorption band and the emission band of some substituted benzaldehydes. This is interpreted as arising from intermolecular association complexes. These complexes are formed in some cases between molecules of the solute and in other cases between molecules of solvent and solute.

The position of the emission band is found not to parallel that of the n-pi absorption band. This arises from increased interaction between the phenyl group and the carbonyl group in the excited state.

Shifts of the emission spectra which in some cases are evidently caused by hydrogen bonded complexes between the solvent and the solute have been recorded. The addition of about 1\% by volume of chloroform to a solution of an aromatic carbonyl compound in hydrocarbon solvent is frequently found to cause an unusually large spectral shift.

Compounds with a hydroxyl group ortho to a carbonyl or a carboxyl group are found, in certain solvents, to begin emitting the expected phosphorescence only after several minutes of excitation. It is postulated that these
substances in the intramolecular hydrogen bonded form do not emit the phosphorescence. The absorption of light, however, converts some of these substances to the unchelated form which then emits normally.
INTRODUCTION

Studies of electronic transitions furnish information which can be useful in the development of theories of electronic structure and molecular reactivity. In addition, such studies can frequently be used to establish empirical methods of identification of molecular species. Absorption spectroscopy and fluorescence spectroscopy of organic substances have been used in these ways for many years.

Both absorption and fluorescence result from transitions between singlet states. Since the identification of transitions involving triplet levels in 1944 (21), studies of these transitions have also received considerable attention (17, 18, 19).

The absorption spectra of aromatic carbonyl compounds usually show three electronic transitions in the near ultraviolet region. The lowest energy of these is attributed to absorption by the carbonyl group under the influence of the benzene ring. The two higher energy transitions probably correspond to the 2550Å and the 1900Å bands found in benzene.
but shifted to longer wavelengths under the influence of the carbonyl group (26).

The present study is concerned almost entirely with electronic transitions associated with the carbonyl group; these are the lowest energy absorption band and the emission band of these compounds. The effects of variations in molecular structure and the effects of various solvents on the lowest energy absorption band have been studied by other workers. A corresponding study of the effects of these variations on the emission band has not been made previously, however.

This research, then, is concerned primarily with the effects of changes in molecular structure and changes in molecular environment on the emission from aromatic carbonyl compounds. Data on the lowest absorption band not previously reported are also presented here.

Normally two emissions, a fluorescence and a phosphorescence, can be obtained from aromatic compounds. However, in the aromatic carbonyl compounds the phosphorescence process occurs to the exclusion of fluorescence.
II

THE LOWEST ENERGY ABSORPTION BAND

Mulliken and McMurray (27, 24, 25) interpreted the low intensity, lowest energy absorption band found in carbonyl compounds as resulting from a transition involving a non-bonding electron localized on the carbonyl oxygen. Transitions of this type are now commonly termed n-pi transitions. They occur in many types of organic compounds containing hetero atoms.

Originally these bands were characterized by their low energy and low intensity, which were in agreement with theoretical considerations (27, 24). But recently Kasha (17), Brealy and Kasha (8), McConnell (23), Bayliss and McRae (1, 2), and Pimentel (31) have discussed the effects of solvent on electronic transitions, particularly n-pi transitions, and it is agreed that n-pi absorption bands are also characterized by a shift to higher energy on changing from a non-polar to a polar solvent.

A second effect of changing from a non-polar to a polar solvent is the blurring of vibrational structure of
the n-pi absorption band. This has been attributed (1) to the very short lifetime of the Franck-Condon excited state. This state is defined below.

The carbonyl oxygen is at the negative end of the molecular dipole and the n-pi absorption results in a decrease in the dipole moment. Light absorption occurs in a shorter time than that required by the solvent molecules to follow this decrease in dipole moment (Franck-Condon Principle), so that in polar solvents the excited molecule immediately after absorption will not be in equilibrium with its environment. The molecule is then in the Franck-Condon excited state. (In a non-polar solvent the solute-solvent forces arise from effects due to dispersion and polarizability. These change quickly enough during absorption to maintain equilibrium.) At normal temperatures equilibrium in polar solvents is established very quickly ($10^{-13}$ to $10^{-11}$ seconds) so that the non-equilibrium state has a very short lifetime. The uncertainty principle then does not permit establishment of vibrational quantization.

On cooling a solution of the carbonyl compound in polar solvent to a rigid glass, vibrational structure develops. The mass hinders molecular rotation, making the lifetime of the Franck-Condon, or non-equilibrium, excited state approach that of the excited state in equilibrium with the
solvent. Vibrational quantization is then established.

The n-pi absorption band of benzaldehyde (Figure 1) in methylcyclohexane (MCH) at room temperature clearly shows vibrational structure. In alcohol this structure disappears and the band peak shifts to higher energy. Cooling of an alcoholic solution causes the vibrational structure to reappear while the band remains at the higher energy.

Steric interaction between parts of the molecule causes blurring of the vibrational structure, even in non-polar solvents. Benzophenone (Figure 2) in methylcyclohexane at room temperature has indistinct structure in its n-pi band due to interference between the 2 and 2' hydrogens. The n-pi band of propiophenone has almost no vibrational structure due to the interference between the alkyl and phenyl groups. On cooling, however, the typical structure appears. The vibrational structure is observed at room temperature in the spectra of compounds which are similar to these, but which are made rigid by formation of a cyclic system. Thus structure is apparent in the n-pi bands of anthrone and α-tetralone (Figure 3). The retention of structure in the n-pi absorption band of o-chlorobenzaldehyde and 2,3-dimethoxybenzaldehyde is evidence for configurations I and II, stabilized through formation of intramolecular hydrogen bonds (32, 33). Otherwise, interaction between the carbonyl
Figure 1. ABSORPTION SPECTRA

a. Benzaldehyde in MCH @ 23° C
b. Benzaldehyde in alcohol @ 23° C
c. Benzaldehyde in EPA @ 77° K
Figure 2. ABSORPTION SPECTRA

a. Benzophenone in MCH @ 23° C
b. Benzophenone in alcohol @ 77° K
c. Propiophenone in MCH @ 23° C
d. Propiophenone in EPA @ 77° K
Figure 3. ABSORPTION SPECTRA

a. Anthrone in MCH @ 23°C
b. α-Tetralone in MCH @ 23°C
c. o-Chlorobenzaldehyde in MCH @ 23°C
d. 2,3-Dimethoxybenzaldehyde in MCH @ 23°C
oxygen and the ortho substituent would be expected to blur the structure in the unchelated form.

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\begin{array}{c}
\text{Cl} \\
\text{H} \\
\text{C} = \text{O}
\end{array} & \quad \begin{array}{c}
\text{O} = \text{H} \\
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_3
\end{array}
\end{align*}
\]

In cases in which the vibrational structure of the n-pi band is resolved (either in non-polar solvents at room temperature or in polar solvents at low temperature), it is found that the vibrational interval is approximately 1,200 cm\(^{-1}\). This same interval is found in the n-pi bands of aliphatic aldehydes where it is assigned to the carbon-oxygen vibration in the excited state. The agreement of this vibrational frequency with the carbon-oxygen single bond stretching frequency and the agreement of the carbon-oxygen bond distance in the excited state with the normal single bond distance has been discussed by Bruck and Scheibe (9). These authors offer configuration III as a model of the ground state and configuration IV as a model of the emitting state, where arrows indicate the lone pair of oxygen p electrons and the pi electrons. The direction of the arrow indicates
the relative spin.

These models emphasize the localization of the n-pi absorption in the carbonyl group where it is influenced to a comparatively small extent by the remainder of the molecule.

An example of the small influence of the remainder of the molecule on the carbonyl absorption is furnished by the spectra of benzaldehyde, furfural, and 2-thiophenaldehyde. Although the higher energy bands of these molecules exhibit considerable differences, the n-pi bands are similar (Figure 4).

In a series of related compounds the position of the n-pi absorption band is determined largely by the electron density on the carbonyl carbon. Since the transition involves a decrease in the molecular dipole moment, the net effect of absorption is the transfer of negative charge away from the carbonyl oxygen. Increasing the electron density on the carbonyl carbon opposes this transition, and moves the
Figure 4. ABSORPTION SPECTRA

a. Benzaldehyde in MCH @ 23° C
b. Furfural in MCH @ 23° C
c. 2-Thiophenealdehyde in MCH @ 23° C
absorption band to higher energies.

Because the electron releasing tendency of alkyl groups is greater than that of hydrogen, the $n$-$\pi$ absorption of the alkyl-aryl ketones is at higher energies than that of the aromatic aldehydes (Figure 5).

The $n$-$\pi$ absorption of acetomesitylene (Figure 5) is at even higher energies, but this primarily reflects the hindrance to planarity of the molecule which decreases conjugation between the phenyl and carbonyl groups. That this is the cause of the absorption moving to higher energy, rather than the above inductive effect, is shown by consideration of the infrared vibrational frequency of the carbonyl group. This is known to decrease with increased conjugation and to decrease with increased polarity of the carbon-oxygen bond (46). Thus the frequency change from 1707 cm$^{-1}$ in benzaldehyde (46) to 1686 cm$^{-1}$ in acetophenone (39) reflects the increased polarity of the carbon-oxygen bond. In acetomesitylene, however, the frequency is 1701 cm$^{-1}$ (39) in accordance with the decrease in conjugation.

The $\pi$-$\pi$ transitions in $p$-methoxybenzophenone occur at lower energies than the corresponding transitions in benzophenone, but the $n$-$\pi$ absorption is shifted to higher energies (10) (Figure 6). Still further shifts of these bands occur in $p,p'$-dimethoxybenzophenone where the $n$-$\pi$ band is
Figure 5. ABSORPTION SPECTRA

a. Benzaldehyde in MCH @ 23°C
b. α-Tetralone in MCH @ 23°C
c. Acetomesitylene in MCH @ 23°C
Figure 6. ABSORPTION SPECTRA

a. Benzophenone in alcohol @ 77° K
b. p-Methoxybenzophenone in alcohol @ 77° K
c. p,p'-Dimethoxybenzophenone in alcohol @ 77° K
nearly covered by the much more intense pi-pi band. These shifts occur because of the electron releasing ability of the methoxy group.

The n-pi absorption band of p-chlorobenzaldehyde (Figure 7) is at lower energies than that of benzaldehyde, reflecting the electron withdrawing ability of chlorine. This band shifts to higher energies in anisaldehyde, again in accord with the inductive effect of the methoxy substituent.

In view of the opposite effects of electron releasing substituents on the positions of the n-pi and the pi-pi bands, it would be anticipated that strongly electron releasing groups would cause the bands to reverse their relative positions. This would amount to a disappearance of the n-pi band as it is covered by the much more intense pi-pi band. This is actually observed in dimethylaminobenzaldehyde, vanillin, and piperonal. In these compounds the lowest absorption band is very intense and has no vibrational structure.

In the absorption spectra of some substituted benzaldehydes (Figure 7), additional structure is found in the n-pi bands. Here, however, the characteristic interval, 1200 cm\(^{-1}\), still occurs, but between alternate rather than adjacent peaks. This doubling of the spectra, which is also
Figure 7. ABSORPTION SPECTRA

a. p-Chlorobenzaldehyde in MCH @ 23° C
b. Benzaldehyde in MCH @ 23° C
c. Anisaldehyde in MCH @ 23° C
Figure 7. ABSORPTION

cm^{-1} \times 10^{-3}
observed in the emission from these compounds, apparently results from formation of intermolecular complexes.

Brealy and Kasha (8) have studied a similar doubling of the n-pi absorption bands of benzophenone and of pyridiazine on addition of small quantities of alcohol to a hydrocarbon solution. The appearance of the new bands was attributed to formation of a complex between the solute and the added alcohol. In the cases considered here the complexes must be formed between molecules of the substituted benzaldehydes as the band doubling is observed in pure hydrocarbon solvents. The question of which substituted benzaldehydes show this doubling in their spectra and a discussion of the emissions obtained from these compounds is deferred to the next section.
Absorption spectroscopy and fluorescence spectroscopy have long been used in the study of electronic transitions of organic molecules between singlet states, but the first identification of transitions involving triplet states in organic molecules was not made until 1944. Terenin (42) in 1943 had postulated the involvement of triplet states in electronic transitions, but made no general identification. Since this original work by Lewis and Kasha (21) the general area of triplet states and inter-system crossing has been intensively studied (17, 18, 19).

In general aromatic carbonyl compounds under the proper conditions (See Part V) emit light quite efficiently. This emission is nearly always a phosphorescence; that is, it results from a transition from the lowest triplet level to the singlet ground level. (However, weak lines have been found in emission from these compounds in the vapor phase, which evidently arise from transitions from the excited singlet state (36, 38).) The reasons for this high probability of
conversion to the triplet state have been discussed by Kasha (18).

Brealy (7) has pointed out the difficulties, which can be caused by impurities, in identification of a phosphorescence with a particular molecular species. It is only in cases in which the quantum yield of phosphorescence is high that an assignment can be unequivocally made on the basis of emission alone. The quantum yields of phosphorescence of benzophenone and of acetophenone have been measured by Gilmore, Gibson, and McClure (14, 15) and have been found to lie between 0.56 and 0.84 at 77°K in an alcoholic solvent. The quantum yields of phosphorescence of other aromatic carbonyl compounds in which the emission is of the n-pi type should also be in this range. Based on this assumption of high quantum yields, it is felt that the assignments made here are valid.

The emission spectra of benzaldehyde (41, 21, 36, 38, 11); acetophenone (41, 46, 11, 36, 22); and benzophenone (21, 22, 12, 11) have been reported by other investigators. The work reported in this chapter is first a study of the phosphorescences obtained from substituted compounds of these types made in order to gain insight into the effects of substituents on the emission spectra of aromatic carbonyl compounds; and second, a study of the influence of solvent on
these emission spectra. Studies of the first type have been reported for alkyl substituted benzenes (28) and for some aromatic nitro-amines (13). Dorr (11) has described the effects of various solvents on the phosphorescence of unsubstituted aromatic carbonyl compounds.

The relative position of the phosphorescence of the unsubstituted carbonyl compounds is found to parallel that of the n-pi absorption bands. That is, the emission from benzaldehyde lies at lower energy than that from acetophenone; the emission from benzophenone is at still lower energy (Figure 8). But, unlike the n-pi absorption bands for a series of substituted aromatic carbonyl compounds (discussed in II), the relative positions of which were found to be related to the inductive effect of the substituent, a more complex relationship is found to govern the position of the emission bands. This increased complexity results from increased interaction between the carbonyl group and the phenyl group in the emitting state. According to the Franck-Condon principle, during absorption the atoms of the molecule being excited do not change their positions appreciably because of the short time involved. Before the molecule emits, however, ample time has passed to allow the molecule to reach the most stable configuration of its excited state. This change in configuration in the excited state and its effect of increasing
Figure 8. PHOSPHORESCENCE SPECTRA

a. Benzophenone in alcohol
b. Benzaldehyde in alcohol
c. Acetophenone in alcohol
interaction between the carbonyl and phenyl groups has been discussed by Bruck and Scheibe (9).

The emissions from benzaldehyde, furfural, and 2-thiophenaldehyde furnish an example of this increased interaction. Although the n-pi absorption bands of these three compounds were found to coincide in energy (Figure 4), the positions of the emission from these compounds vary considerably (Figure 9).

The phosphorescence spectra of aromatic carbonyl compounds have a banded structure (Figure 8) with an interval of approximately 1650 cm\(^{-1}\) between the bands. This frequency agrees well with the carbonyl stretching frequency found for these molecules in the ground state.

Another characteristic of the compounds studied here is that under certain conditions they generally have a second phosphorescence. Terenin (41) reported a different emission from benzaldehyde crystals obtained from solutions of this compound. Later, Ferguson and Tinson (12) reported a new emission from benzophenone in hydrocarbon solvents, the intensity of which was concentration dependent. Terenin and Ermolaev (43) suggested that this emission was from microcrystals of benzophenone formed at liquid nitrogen temperature. In the present work it was observed that the emission from crystals of benzophenone was identical with that from
Figure 9. PHOSPHORESCENCE SPECTRA

a. 2-Thiophenaldehyde in alcohol
b. Furfural in alcohol
c. Benzaldehyde in alcohol
the concentrated hydrocarbon solutions. (McClure (22), however, has obtained the emission characteristic of dilute solutions from freshly sublimed crystals of benzophenone. He points out that different crystal emissions may be expected since benzophenone is known to exist in several crystalline forms).

Emission characteristic of the crystalline state was generally observed in this study in relatively concentrated solutions of aromatic carbonyl compounds \((10^{-2} \text{ molar})\) in hydrocarbon solvents (even though the glass formed could be quite clear). By making the hydrocarbon solution sufficiently dilute \((10^{-5} \text{ molar})\) an emission very similar to that obtained from solutions in polar solvents was obtained. For solutions of intermediate concentration, both emissions could be recorded simultaneously. Figure 10 shows the spectra obtained from acetophenone. These emissions which are attributed to the crystalline state will not be considered further here, and all emissions reported from solutions using hydrocarbon solvents are from solutions sufficiently dilute that the crystal emission does not appear.

Other characteristics distinguishing the phosphorescences of aromatic carbonyl compounds are the short lifetime of the emitting state and the small splitting between the first excited singlet and the lowest triplet levels.
Figure 10. PHOSPHORESCENCE SPECTRA

a. Acetophenone crystal
b. Acetophenone in petroleum ether (concentrated)
c. Acetophenone in petroleum ether (dilute)
Usually the lifetime of the phosphorescence of organic molecules is in the range, tenths of seconds to seconds, but the lifetime of phosphorescence of the carbonyl compounds is usually found to be several milliseconds \((14, 15, 11)\). The splitting between the lowest energy singlet - singlet absorption band and the triplet-singlet emission band in simple aromatic hydrocarbons is well over \(10,000 \text{ cm}^{-1}\) but in the carbonyl compounds this splitting is usually well under \(5,000 \text{ cm}^{-1}\) \((17)\). Sidman \((40)\) has given a theoretical treatment of the electronic structure of the carbonyl group which considers these points.

The high probability of conversion to the triplet state, the short lifetime of the triplet state and the small interval between the lowest energy excited singlet level and the triplet level all result from a greater breakdown of the spin selection rule in aromatic carbonyl compounds than is normally found in organic molecules.

**B. Benzaldehyde and related compounds**

Phosphorescences from benzaldehyde and related compounds show two types of structure. Benzaldehyde, o-chlorobenzaldehyde, and salicylaldehyde in petroleum ether \((\text{Figure 11})\) have emissions with vibrational bands spaced about \(1700 \text{ cm}^{-1}\) apart; this is in good agreement with the carbonyl.
Figure 11. PHOSPHORESCENCE SPECTRA

- a. Salicylaldehyde in petroleum ether
- b. o-Chlorobenzaldehyde in petroleum ether
- c. Benzaldehyde in petroleum ether

\[ \text{cm}^{-1} \times 10^{-3} \]
stretching frequency found in these molecules in the ground state. Other aldehydes studied have emissions which show a more complex band structure, apparently made up of two sets of bands with this spacing; that is, alternate rather than adjacent bands are spaced about 1700 cm$^{-1}$ apart.

This doubling of the spectra, found also in the n-pi absorption band, was discussed previously (page 15) and was attributed to formation of intermolecular complexes. This doubling is found to be prominent in the emission from compounds which would be expected to have a tendency to associate. Thus the emission from a p-hydroxybenzaldehyde (Figure 14) always shows the double structure, while the emission from salicylaldehyde (Figure 11), which in hydrocarbon solvents exists as unassociated molecules due to stabilization of this form through intramolecular hydrogen bonds, is of the normal type. Similar differences occur between the spectra of p-chloro and o-chlorobenzaldehyde. The ortho compound is also stabilized through an intramolecular hydrogen bond (32, 33) (Page 9).

A change to a polar solvent frequently causes compounds which have normal emissions in non-polar solvents to emit the double structure. See for example the emission of salicylaldehyde in alcohol (Figure 23), the emission of o-chlorobenzaldehyde in chloroform-petroleum ether (Figure 12),
Figure 12. PHOSPHORESCENCE SPECTRA

a. o-Chlorobenzaldehyde in petroleum ether
b. o-Chlorobenzaldehyde in alcohol
c. o-Chlorobenzaldehyde in petroleum ether-chloroform
d. p-Chlorobenzaldehyde in petroleum ether
e. p-Chlorobenzaldehyde in alcohol
f. p-Chlorobenzaldehyde in petroleum ether-chloroform
PLATE BLACKENING

Figure 12.
or the emission of benzaldehyde in chloroform-petroleum ether (Figure 13). Evidently then the complexing of the aldehyde with a polar solvent, which must occur in the cases just mentioned, affects the spectra of these compounds in a way quite similar to the way it is affected by intermolecular complexing between molecules of the aldehyde. The latter must occur, for example, in solutions of p-hydroxybenzaldehyde in hydrocarbon solvents.

The nature of the complex formed cannot be clearly determined from the data obtained here. In most cases a hydrogen bonded complex through the carbonyl oxygen seems to be very probable, but in other cases (e.g. anisaldehyde in petroleum ether (Figure 14)), the nature of the complex responsible for the double structure in the spectra is less definite. The possibility of a hydrogen bond through the aldehyde hydrogen is not ruled out, however. Terenin has postulated the existence of such intermolecular bonds and, as mentioned earlier, existence of intramolecular bonds through the aldehyde hydrogen has been demonstrated experimentally (32, 33). In this study of carbonyl compounds the formation of complexes between molecules of the solute is indicated only in the case of the aldehydes. This also possibly indicates involvement of the aldehyde hydrogen in formation of these complexes.
Figure 13. PHOSPHORESCENCE SPECTRA

- a. Benzaldehyde in petroleum ether
- b. Benzaldehyde in alcohol
- c. Benzaldehyde in petroleum ether-chloroform
If the complex emission discussed above arose from molecules in two different environments (associated and un-associated molecules) it should be possible to change the relative intensity of the two sets of bands in a given solvent-solute system by modifying the experimental conditions. The system studied was salicyaldehyde in alcohol. No change in the emission was obtained, however, by varying the energy of the exciting light or the time of exposure to the exciting radiation prior to recording the emission. These would be expected to alter the emission if the absorption spectra in the two environments were different, or if the distribution of molecules between the environments could be changed by the incident radiation (see Section IV). Perhaps the variations were not great enough to alter the emission appreciably. Attempts to alter the recorded relative intensities by varying the speed of the phosphoroscope were also unsuccessful. This variation would be expected to alter the recorded spectra if the lifetimes of the excited states were different.

The emission from p-chlorobenzaldehyde in hydrocarbon solvents is at a higher energy than that from the ortho chloro compound (Figure 12). This relationship is preserved in solvents containing alcohol and, as occurs fairly generally, the vibrational bands become slightly broader. But a
surprising result is obtained using a hydrocarbon solvent containing about 1% chloroform. It is found that the relative position of the emissions is reversed. The emission from the para compound is at a lower energy in this solvent than in any other, while the emission from o-chlorobenzaldehyde occurs at a higher energy. New bands appear in the emission from the ortho compound in this solvent.

In this study appreciable changes in the emission spectra of aromatic carbonyl compounds have been frequently found in changing from a pure hydrocarbon solvent to one containing a small quantity of chloroform. It can be concluded from the amount of chloroform in the solvent that the bulk properties of the solvent are not altered appreciably. This change in emission must then result from formation of a hydrogen bonded complex at the low temperatures.

Perhaps the most surprising result is not the large effect of addition of small amounts of chloroform to hydrocarbon solvents, but the much smaller effect of similar quantities of alcohol. The alcohol should certainly form stronger hydrogen bonds than the chloroform, and that this is the case is indicated by the fact that addition of chloroform to alcoholic solvents does not alter the emission. (Evidence that the alcohol forms complexes with carbonyl compounds is furnished by the identity of the carbonyl emissions
from solutions containing 1% alcohol and those from pure alcohol.)

The phosphorescence of benzaldehyde shifts only slightly with changes in solvent (Figure 13), but in chloroform-hydrocarbons solvent new bands appear. A spectrum very similar to that obtained from the 1% chloroform solution has been reported from solutions of benzaldehyde in alcohol-water solvent mixtures (11). In the present study it was observed that the change in the emission of an aromatic carbonyl compound on changing from a hydrocarbon to a chloroform-hydrocarbon solvent is quite similar to that observed by others upon adding water to an alcoholic solution. Additional examples of this are given later.

The emission from p-hydroxybenzaldehyde (Figure 14) is much the same in hydrocarbon, chloroform-hydrocarbon, and alcoholic solvents, but the emission from a hydrocarbon solvent containing 1% diethylether is found at appreciably higher energies. This must be the result of hydrogen bonding between the hydroxyl group of the aldehyde and an ether molecule.

Anisaldehyde (Figure 14) emits at a higher energy than p-hydroxybenzaldehyde. The emission from this compound in ether-hydrocarbon solvents does not change appreciably from that obtained from petroleum ether. This would be
Figure 14. PHOSPHORESCENCE SPECTRA

- a. p-Hydroxybenzaldehyde in petroleum ether
- b. p-Hydroxybenzaldehyde in petroleum ether-alcohol
- c. p-Hydroxybenzaldehyde in petroleum ether
- d. Anisaldehyde in petroleum ether-ether
expected since anisaldehyde cannot form hydrogen bonds with the ether.

2,4-dihydroxybenzaldehyde (Figure 15) is the only substituted benzaldehyde investigated which emits at a higher energy than benzaldehyde itself. Emission from this compound is discussed further in Section IV.

In the absorption spectra of vanillin, piperonal, and p-dimethylaminobenzaldehyde, as discussed earlier (page 15), the n-pi absorption was completely covered by the more intense pi-pi absorption. The emissions from these compounds (Figure 16) also differ from the characteristic carbonyl emission. The vibrational structure is different and the lifetime of the excited states appear longer. The emissions are similar to that from the negative ion of p-hydroxybenzaldehyde formed in an ammonium hydroxide-alcohol solvent. The o' substituent, like the amino group, has strong electron releasing properties and therefore the same type of spectra are expected.

The spectra of 2,3-dimethoxybenzaldehyde differ both in absorption (Figure 3) and emission (Figure 15) from those of 3-methoxy-4-hydroxy benzaldehyde (vanillin). In the former compound the lowest energy absorption band is an n-pi band and the emission from this compound is the typical carbonyl emission. But in vanillin the lowest energy absorption band
Figure 15. PHOSPHORESCENCE SPECTRA

a. 2,3-Dimethoxybenzaldehyde in alcohol
b. 2,4-Dihydroxybenzaldehyde in alcohol
Figure 16. PHOSPHORESCENCE SPECTRA

a. p-Dimethylanobenzaldehyde in alcohol
b. p-Dimethylanobenzaldehyde in petroleum ether
c. Vanillin in alcohol
d. Piperonal in alcohol
e. p-Hydroxybenzaldehyde in alcohol-ammonium hydroxide
is a pi-pi band, while the emission is of the type described in the preceding paragraph. These differences can be attributed to the decrease, in the 2,3-dimethoxy compound, of conjugation between the 2-methoxy group and the phenyl ring caused by steric interference. The 2-methoxy group is forced out of the plane of the ring by crowding with the carbonyl group on one side and with the 3-methoxy group on the other. As a result of this decreased conjugation the n-pi band remains the lowest singlet energy absorption band and the emission shows the typical carbonyl structure.

No emission was obtained from m- or p-nitrobenzaldehyde.

Terenin (41) noted the similarity of emission spectra from many aromatic hydrocarbons, reported by early workers, to that he obtained from benzaldehyde. He attributed the emissions obtained from the hydrocarbons to the impurities resulting from the formation of small quantities of auto-oxidation products. These then emit brightly in dilute solutions. This accounted for these emissions nearly always being in the blue region of the spectrum and for their characteristic carbonyl vibrational structure. In particular, he cited the work of Kronenberger (20), who studied emissions from o-, m-, and p-xylene. Terenin suggested the emissions obtained are actually from o-, m-, and p-tolualdehyde.
formed in small quantities by auto-oxidation of the original xylenes.

More recently Biswas (3, 4, 5, 6) has studied emissions from o-, m-, and p-chloro and bromo-toluenes. Table I compares the emission bands obtained by Biswas from o- and p-chlorotoluene with those obtained from o- and p-chlorobenzaldehyde here. The agreement is good and it is felt that the emissions obtained by Biswas are from the aldehydes produced by auto-oxidation of the substituted toluenes. This interpretation also explains the fact that Biswas could excite the emissions by wavelengths longer than those absorbed by the toluenes (4).

C. Benzophenone and related compounds

The n-pi absorption bands of benzophenone, its p-methoxy and p, p'-dimethoxy derivatives were discussed in section II (Figure 6). The emissions from these compounds all show the typical aromatic carbonyl phosphorescence (Figure 17), but their positions fall in a peculiar order. The emission from benzophenone lies between that of the p-methoxy compound at lower energy and that of the p, p'-dimethoxy compound at higher energy. The emission from p, p'-dihydroxy-benzophenone is the same as that from its dimethoxy analogue.

Figure 18 shows the emission obtained from benzophenone in various solvents. The emission using the 1%
A Comparison of Frequencies Emitted by o- and p-chlorobenzaldehyde with those Reported for o- and p-chlorotoluene.

<table>
<thead>
<tr>
<th>p-chlorobenzaldehyde (in petroleum ether)</th>
<th>p-chlorobenzaldehyde (in chloroform-petroleum ether)</th>
<th>p-chlorobenzaldehyde (in alcohol)</th>
<th>p-chlorotoluene (crystals)</th>
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<td>19,152 (vw)</td>
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Figure 17. PHOSPHORESCENCE SPECTRA

a. p,p'-Dimethoxybenzophenone in petroleum ether
b. Benzophenone in petroleum ether
c. p-Methoxybenzophenone in petroleum ether
Figure 18. PHOSPHORESCENCE SPECTRA

a. Benzophenone in PH
b. Benzophenone in toluene
c. Benzophenone in petroleum ether-alcohol
d. Benzophenone in petroleum ether-chloroform
e. Benzophenone in water glycol
alcohol-petroleum ether solvent is the same as obtained with pure alcohol. The emission using the water-glycol solvent is the same as obtained with water-alcohol solvents (11). The large effect caused by a small amount of chloroform is again apparent.

The benzophenone molecule is forced into a non-planar configuration by repulsion between the 2 and 2' hydrogen atoms. In anthrone these hydrogen atoms are replaced by a methylene bridge which holds the molecule in the planar form. The effects of this structural change on the ultraviolet absorption spectra have been discussed by Jones (16). The increased resonance in the planar molecule shifts the pi-pi absorption bands to longer wavelengths; the n-pi band is also shifted to a slightly lower energy (Compare Figures 2 and 3). The emission band, however, is shifted to higher energy (Compare Figures 18 and 19).

Xanthone, with an oxygen bridge between the two rings, emits at an energy intermediate between that of benzophenone and anthrone.

Anthraquinone also emits the aromatic carbonyl type phosphorescence but at lower energy.

Fluorenone, a compound closely related to the above bridged, benzophenone-like substances, is peculiar in that it has no phosphorescence. Instead, fluorenone emits a
Figure 19. PHOSPHORESCENCE SPECTRA

a. Anthraquinone in alcohol
b. Xanthone in alcohol
c. Anthrone in alcohol
Figure 19.

PLATE BLACKENING

cm$^{-1} \times 10^{-3}$

- a

- b

- c
structureless fluorescence band in the green region of the spectrum (11). In addition, the absorption spectrum of this compound is quite different from that of anthrone and benzophenone (16). There are two possible causes of the anomalous behavior of this compound. First, conjugation may occur between the phenyl rings in fluorenone through the bridging bond, whereas in anthrone the methylene group prevents this type conjugation. Second, the five membered ring in fluorenone is highly strained; this affects the electronic distribution in the carbonyl group, causing the unusually high carbonyl stretching frequency found in this compound (46). Either or both of these affects, conjugation and strain, could be responsible for the change in the type of electronic transitions observed.

As in the case of the substituted benzaldehydes, introduction of strong electron releasing groups apparently changes the nature of the low energy emission. The phosphorescences of p-amino-, p,p'-diamino-, and p,p'-bis (dimethylamino)-benzophenones are practically identical, and consist of a broad structureless band in the green region of the spectrum. The p-amino compound also emits a structureless fluorescence band in the blue region of the spectrum. The highest energy in fluorescence and the lowest energy in absorption occur at about 4020Å.
D. Alkyl-aryl ketones

The emissions from various alkyl-phenyl ketones are all at about the same energy, as would be expected, but the structures of the emissions show an unexpected variation. The emission from acetophenone in alcohol (Figure 20) shows once more the typical carbonyl phosphorescence. Replacement of an Ω-hydrogen by chlorine (phenacyl chloride), however, apparently splits the vibrational bands. This splitting also occurs when the Ω-hydrogen is replaced by a methyl group (propiophenone). Since the chlorine and the methyl group have opposite inductive effects, this splitting is evidently caused, not by electronic factors, but by steric effects.

Spectra identical with that obtained from propiophenone are obtained from butyrophenone, θ-benzoylpropionic acid, the θ-benzoylpropionate ion, 1,4-dibenzoylbutane, and caprylophenone. Evidently then, substituents on the θ-carbon have no further effect on the emission.

The emission from Ω-tetralone (Figure 21) does not show the splitting, but instead has the simple structure consisting of bands spaced at about 1650 cm⁻¹. This fits with the interpretation that the splitting is caused by steric effects since in Ω-tetralone the molecule is made rigid by formation of a cyclic system.
Figure 20. PHOSPHORESCENCE SPECTRA

a. Acetophenone in alcohol
b. Phenacylchloride in alcohol
c. Propiophenone in alcohol
d. Caprylophenone in alcohol
Figure 21. PHOSPHORESCENCE SPECTRA

a. \(\omega,\omega\)-Dibenzylacetophenone in petroleum ether
b. Benzoin in petroleum ether
c. \(\alpha\)-Tetralone in petroleum ether
The emissions from \( \omega,\omega \)-dibenzylacetophenone and from benzoin also do not show the splitting. This may be connected with the replacement of two \( \alpha \)-hydrogens in these compounds by substituent groups, but more probably, like tetralone, the molecules are more rigid. This may be caused in benzoin by formation of an intramolecular hydrogen bond, and in \( \omega,\omega \)-dibenzyl acetophenone by crowding between parts of the molecule which prevents rotation about the bond to the carbonyl carbon atom. In this latter molecule vibrational structure in the \( n-\pi \) absorption band is apparent at room temperature. This is not usually observed in aromatic ketones (See section II) and also indicates a rigid structure.

Emission from acetomesitylene (Figure 22) consists of very broad bands probably resulting from the steric hindrance between methyl groups. Despite the fact that the molecule cannot be planar, which must inhibit resonance between the phenyl and carbonyl groups, the emission occurs at about the same energy as in the ketones discussed above.

The emission from p-chloroacetophenone occurs at a higher energy than that from the p-methoxy compound (Figure 22). The vibrational structure is also sharper in the chloro compound. These same relationships were observed in the analogous benzaldehydes (Part B).
Figure 22. PHOSPHORESCENCE SPECTRA

a. p-Methoxyacetophenone in alcohol
b. p-Chloroacetophenone in alcohol
c. Acetomesitylene in alcohol
of light, however, can convert a molecule to the unchelated form.

Valyashko and Valyashko (45), using the ultraviolet absorption data of Morton and Stubbs (26), have calculated that about 60% of the salicylaldehyde molecules in an alcoholic solution exist in the conjugated chelate form, whereas in hexane at least 92.5% of the molecules are in this form. These data are obtained at room temperature; lowering the temperature should shift the equilibrium in hexane even further to the chelated form. These authors have also studied 5-bromo-salicylaldehyde and 3,5-dibromosalicylaldehyde in alcohol and hexane. They find the equilibrium of the 5-bromo compound shifted even further toward the conjugated chelate form. The position of the equilibrium of the 3,5-dibromo compound is between that of 5-bromosalicylaldehyde and salicylaldehyde. These observations are explained as follows; in the 5-bromo compound the bromine para to the hydroxyl group increases the electronegativity of the hydroxyl oxygen, strengthening the intramolecular hydrogen bond. In the 3,5-dibromo compound this effect is partially cancelled by the tendency of the hydroxyl group to hydrogen bond with the bromine ortho to it.

In the experiments with salicylaldehyde in hydrocarbon solvents, where practically all of the molecules are
CONJUGATED CHELATE SYSTEMS

Rasmussen, Tunnicliff and Brattain (34) have pointed out that ketones containing the structural system

![Chemical Structure](attachment:structure.png)

have abnormal spectroscopic properties. The infrared stretching bands of both the OH and the CO groups are displaced to unusually low frequencies. Further, these authors point out that the ultraviolet absorption spectrum of acetyl acetone is quite different from that of conjugated ketones, but upon acetylation (which destroys system I) the absorption spectrum is converted to this type. Similar spectroscopic effects have been noted in carboxylic acid derivatives (35). These effects are attributed to the influence of the structural system I, termed (34) the conjugated chelate system.

M. Tsuboi (44) has studied a wider variety of similar compounds and found these effects to be quite general,
even occurring in long chain hydrogen bonded proteins

... HN-C = 0 ... HN-C = 0 ...

II

Tsuboi attributes these unexpected spectroscopic properties to the existence of conjugation across the hydrogen bond.

Further evidence which indicates a difference between the conjugate chelate system and the ordinary hydrogen bond has been obtained in the present work. In substances which contain the conjugated chelate system, the appearance of phosphorescence was found to be delayed or was not observed. That is, the majority, if not all, of the molecules had to absorb at least two quanta of light before beginning to emit. For example, the blue phosphorescence of salicylaldehyde in petroleum ether (or other hydrocarbon solvent) becomes visible only after about a two minute exposure to the full intensity of the A-H6 arc. After about a ten minute exposure the emission is fairly bright. These results are understandable if two assumptions are made:

(1) In the conjugated chelate form a molecule does not emit the phosphorescence characteristic of aromatic carbonyl compounds.

(2) In certain solvents at low temperatures these compounds exist almost entirely in the conjugated chelate form. Absorption
in the chelated form, there is no light emission on first exposing the sample to the exciting radiation. The intensity of the emission, however, builds up gradually on continued exposure as some of the molecules are converted to the non-chelated form. In the alcoholic solution, as an appreciable portion of the molecules are already in the non-chelated form, the emission is immediate.

The mechanism proposed by Norman and Porter (29) for the production and trapping of radicals can be applied here to the conversion of chelated to non-chelated systems. According to this mechanism, the energy absorbed by the molecule is sufficient not only to break the bond concerned (in this case the intramolecular hydrogen bond), but also to soften the glass by interaction of the excited molecule with the solvent. This allows the two fragments, or in the present case substituted groups, to move apart. The glass becomes rigid before the fragments can re-combine. (Here, before the chelate system can reform.)

The phosphorescence of salicylaldehyde (Figure 23) is delayed in petroleum ether solution and in petroleum ether containing a small amount of chloroform. The vibrational structure differs in the two solutions. The spectrum from salicylaldehyde in the chloroform containing solvent is similar to the spectrum obtained from the compound in alcoholic solvents.
Figure 23. PHOSPHORESCENCE SPECTRA

a. Salicylaldehyde in petroleum ether (Delayed emission)

b. Salicylaldehyde in petroleum ether-chloroform (Delayed emission)

c. Salicylaldehyde in petroleum ether-ether

d. Salicylaldehyde in alcohol
The emission from the compound in petroleum ether solution containing a small amount of ether is immediate and is quite similar to the emission from alcoholic solutions. Apparently then, the hydrogen bond formed between the ether and the hydroxyl group of salicylaldehyde is strong enough to shift the equilibrium appreciably toward the non-chelated form, whereas the bond between chloroform and the carbonyl group is too weak to do this.

The emission from crystals of salicylaldehyde is immediate and is quite similar to that obtained from solutions in polar solvents. Apparently then, crystals of salicylaldehyde contain some molecules in the non-chelated form.

Similar results are obtained with 2,4-dihydroxybenzaldehyde (Figure 24), only here the vibrational structure is the same in polar and non-polar solvents. This probably reflects the ability of the compound to associate through the 4-hydroxyl group (See page 15), even when in the chelated form.

Salicylic acid, because of the increased electron density on the carbonyl double bonded oxygen, would be expected to form a stronger intramolecular hydrogen bond than salicylaldehyde. This expectation is borne out by the observation that the phosphorescence of salicylic acid and its
Figure 24. PHOSPHORESCENCE SPECTRA

a. 2,4-Dihydroxybenzaldehyde in petroleum ether (Delayed emission)
b. 2,4-Dihydroxybenzaldehyde in alcohol
esters is delayed even in alcoholic solution.

The phosphorescent emission spectra of salicylic acid (Figure 25) and its esters are quite similar to that of ortho-methoxybenzoic acid. In the latter compound no conjugated chelate system is possible, and the emission is observed immediately in all solvents tried.

Weller (48, 49) has investigated the fluorescence of salicylic acid and o-methoxybenzoic acid. These are surprising in that the fluorescence of salicylic acid is blue but that of its methoxy analogue is entirely in the ultraviolet. The absorption spectra are quite similar. Weller attributes the blue fluorescence to the zwitter ion (III) formed in the excited state,

\[
\begin{align*}
H & \overset{\epsilon}{\text{C}} \overset{\epsilon}{\text{O}} \\
\overset{\epsilon}{\text{H}} & \overset{\epsilon}{\text{O}} \\
\overset{\epsilon}{\text{O}} & \overset{\epsilon}{\text{H}}
\end{align*}
\]

III

and by this means accounts for the unusually large energy gap between the lowest energy absorption and the highest energy fluorescence. Weller finds also solutions of salicylic acid at room temperature have a low intensity, ultraviolet fluorescence which corresponds to the fluorescence of the related methoxy compound. This fluorescence disappears
Figure 25. PHOSPHORESCENCE SPECTRA

a. p-Hydroxybenzoic acid in alcohol
b. Salicylic acid in alcohol (Delayed emission)
at low temperatures. These data fit well with those reported here. The zwitter ion (which fluoresces blue) is easily formed from the chelated system, but not from the unchelated form (which fluoresces in the ultraviolet). Then, the disappearance of the ultraviolet fluorescence on cooling corresponds to nearly complete conversion of salicylic acid to the chelated form.

Salicylic acid then in the chelated form emits the blue fluorescence of its zwitter ion (III). In the unchelated form it emits fluorescence in the ultraviolet and phosphorescence in the blue, just as its methoxy analogue. The ultraviolet fluorescence of the hydroxy compound in rigid glasses should then appear simultaneously with the delayed blue phosphorescence.

The loss of structure in the emission from ortho substituted benzoic acids (not observed in emission from ortho substituted benzaldehydes) is probably due to increased crowding of the doubly bound oxygen. The emission from p-hydroxybenzoic acid (Figure 25) is at about the same energy, and shows the structure normally found in the emission from benzoic acid and substituted benzoic acids.

Table II summarizes the results obtained in this study of compounds capable of forming the conjugated chelate
<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission in hydrocarbon solvent</th>
<th>Emission in alcoholic solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylaldehyde</td>
<td>Delayed</td>
<td>Immediate</td>
</tr>
<tr>
<td>2,4-Dihydroxybenzaldehyde</td>
<td>Delayed</td>
<td>Immediate</td>
</tr>
<tr>
<td>5-Chloro-2-hydroxybenzophenone</td>
<td>Immediate</td>
<td>Immediate</td>
</tr>
<tr>
<td>2,4-Dibenzoylresorcinol</td>
<td></td>
<td>Delayed</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td></td>
<td>Delayed</td>
</tr>
<tr>
<td>Phenyl salicylate</td>
<td></td>
<td>Delayed</td>
</tr>
<tr>
<td>p-ter-butyl phenyl salicylate</td>
<td></td>
<td>Delayed</td>
</tr>
<tr>
<td>Dibenzoylmethane</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>Benzoylecetone</td>
<td></td>
<td>None</td>
</tr>
</tbody>
</table>
Only the results obtained with 5-chloro-2-hydroxybenzophenone are not in accord with the proposed interpretation. The emission from this compound is immediate, even in hydrocarbon solvents, and is quite similar to that of benzophenone. The compound was purified by dissolving in sodium hydroxide, then precipitating with hydrochloric acid, followed by several re-crystallizations from petroleum ether, but the emission spectrum remained unchanged. The possibility of the presence of an isomer of the 5-chloro-2-hydroxy compound was not eliminated.

The emission from 2,4-dibenzoyl resorcinol in alcohol appears quite slowly and after 40 minutes exposure to the exciting radiation it is still quite weak. In this compound (IV) substituents with like inductive effects are meta to each other, while those with opposite inductive effects are either ortho or para to each other. Thus, the inductive effects are enhanced, lowering the electron density on the hydroxyl oxygens and increasing it on the carboxyl oxygens. This strengthens the intramolecular
hydrogen bonds and accounts for the slow appearance of the phosphorescence.

In molecules containing the conjugated system (V)

\[
\begin{align*}
  &\text{V} \\
  &\text{C}=\text{C}<\text{C}=\text{O}
\end{align*}
\]

phosphorescence appears to lie at the red edge of the visible region. It appears weak to the eye, either because it actually is weak, or because it is located largely in a region to which the eye is not sensitive. An emission of this type has not been photographed, but has been observed in benzalacetone and \( p,p' \)-dichlorobenzalacetophenone. In dibenzoyl methane and benzoylacetonone, which exist almost entirely in the enol form and which possess the conjugated system \( V \), no emission is observed. These compounds can also form the conjugated chelate system. In the compound 1,3-indanedione, which in the enol form also has the conjugated system \( V \), but which cannot form the chelate system due to its cyclic structure, the red phosphorescence is immediate.

Aromatic compounds containing a hydroxyl group ortho to a carboxyl or carbonyl group have long been used for stabilizing plastics against photodeterioration. This is understandable in view of the interpretation proposed here whereby
light absorption may result in destruction of the conjugated chelate system, but still leaves an unreactive, stable molecule.
V

EXPERIMENTAL PROCEDURE

At room temperature the loss of excitation energy from the metastable triplet state through thermal collisions is so probable, because of the long lifetime of this state, that, normally, phosphorescence cannot be observed. As the temperature is lowered and as the solvent containing the substance of interest becomes more viscous, loss of energy through thermal collisions becomes less probable and phosphorescence can be observed. All phosphorescences reported here were obtained from rigid glassy solutions at liquid nitrogen temperature.

Also as a result of the long lifetime of the triplet state, it is possible to mechanically separate the exciting from the emitted light. This is accomplished here using a phosphoroscope consisting of two rotating vanes. The vanes alternately expose the sample to the exciting light while blocking the light from the spectrograph, then expose the sample to the spectrograph while blocking the exciting light.

Most of the compounds used in this study were obtained commercially. Phenyl salicylate, p-terbutyl salicylate,
5-chloro-2-hydroxybenzophenone and 2,4-dibenzoylresorcinol were donated by Dow Chemical Company. The caprylophenone was donated by Mr. Estorge Sabille of these laboratories, who synthesized the compound in the course of another investigation. Tetralone was prepared by air oxidation of tetralin (37). Purifications, when they seemed necessary, were made by solvent extraction, vacuum distillation and/or recrystallization. As would be anticipated from the high quantum yields of phosphorescence of these compounds, impurities did not present as big a problem as normally encountered in work of this kind. In no case was an emission spectrum altered by purification.

Solvents used in this study included either pure, or in various combinations, absolute ethanol, anhydrous ethyl ether, ethylene glycol, isopentane, petroleum ether "A," methyl cyclohexane, methyl cyclopentane, chloroform (reagent grade) and ammonium hydroxide (reagent grade). Absolute ethanol, anhydrous ethyl ether, chloroform, and ammonium hydroxide were used without further purification. Hydrocarbon solvents were used in certain cases without further purification, but in other cases were purified by washing with concentrated sulfuric acid, washing with sodium carbonate solution, washing with water, drying over magnesium sulfate and finally distilling. Except when using hydrocarbon solvents purified
as outlined above, a weak phosphorescence was emitted by the solvent itself. These solvent emissions, however, required exposures over 10 times as long as those used to photograph emissions from the carbonyl compounds (2 hours vs. 10 minutes). The solvent emissions therefore do not affect the data reported here.

The following solvents which form glasses at liquid nitrogen temperature were used:

1) EPA, a mixture by volume of 5 parts anhydrous ether, 5 parts isopentane and 2 parts absolute ethanol;
2) PH, a 1:1 mixture by volume of methyl cyclopentane and methyl cyclohexane;
3) pure petroleum ether "A;"
4) absolute ethanol;
5) a 2:1 mixture by volume of ethylene glycol and water;
6) 1% by volume of chloroform in petroleum ether "A;"
7) 1% by volume of ether in petroleum ether "A;"
8) 1% by volume of carbon tetrachloride in petroleum ether "A;"
9) 1% by volume of absolute alcohol in petroleum ether "A;" and
10) a 1:4 mixture by volume of ammonium hydroxide and absolute alcohol.

The solvents numbered 4, 5, and 10 above cracked extensively at liquid nitrogen temperature. This fracturing cut down the intensity of light entering the spectrograph (by scattering both the incident and emitted light); but this effect was minimized by using small (1 cm. diameter) quartz test tubes.

Phosphorescences and low temperature absorptions were photographed with a Bausch and Lomb medium quartz spectrograph. A General Electric A-H6 high pressure mercury arc with a quartz jacket was used to excite the phosphorescences. A Hanovia 71-3 hydrogen discharge tube provided a continuous spectrum for absorption work.

All low temperature emissions and absorptions were recorded on Eastman Spectroscopic plates. Plates were calibrated with lines of the mercury and/or helium spectra. The plates were traced using a Leeds and Northrup recording microphotometer. Drawings made from tracings of the plates have arbitrary scales along the ordinate and the intensities of the different spectra are not comparable.

The room temperature absorptions were obtained using a Beckman Model DK-1 Recording Spectrophotometer.
Further details of the experimental procedure are given in an earlier dissertation from this laboratory (30).
VI

SUMMARY

This research is concerned with electronic transitions associated with the carbonyl group of aromatic carbonyl compounds. These transitions are the lowest energy absorption band and the phosphorescence emission band. The emission spectra of more than thirty compounds of this type are given.

The lowest energy absorption band results from an n-pi transition. The position of this band is found to be determined by the electron density on the carbonyl carbon atom. As the substituents attached to this atom become more electron releasing the n-pi transition moves to higher energy. Conversely, electron withdrawing substituents lower the energy of the n-pi transition. This relationship is shown to govern the position of the n-pi transition in a series of substituted benzaldehydes and in a series of substituted benzophenones.

In many of the substituted benzaldehydes, doubling of the vibrational structure is found in both the n-pi absorption band and in the emission band. This is attributed to
the existence of intermolecular complexes which are formed in some cases between molecules of the solute and in other cases between molecules of the solute and solvent.

The position of the emission band is found not to parallel that of the n-pi absorption band. Increased interaction between the phenyl group and the carbonyl group in the excited state accounts for this behavior. Thus the absorption bands of benzaldehyde, furfural, and thiophenaldehyde are at very nearly the same energy, but the emission bands are at quite different energies. Other examples illustrating the effects of this increased interaction in the excited state are given.

Solvents which form hydrogen bonds with the carbonyl compounds are found to cause appreciable shifts in the energy of the emission spectra of these substances. Emission from the carbonyl compound in a hydrocarbon solvent containing about 1% chloroform is frequently found to have been shifted an unusual amount with respect to its position in pure hydrocarbon solvents.

Aromatic carbonyl compounds which have a hydroxyl group ortho to the carbonyl group are found, under certain conditions, to begin emitting the typical phosphorescence only after several minutes of excitation. This behavior is explained by assuming:

1. In the intramolecular hydrogen bonded form
a molecule does not emit the phosphorescence characteristic of aromatic carbonyl compounds.

2. In certain solvents at low temperatures these compounds exist almost entirely in the intramolecular hydrogen bonded form. Absorption of light, however, can convert a molecule to the non-hydrogen bonded form.
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VIII

VITA

Sam Stewart Mims was born April 10, 1931, in Easley, South Carolina. He attended public schools in Minden and Baton Rouge, Louisiana and graduated in 1948 from University High School in Baton Rouge. He attended Clemson College from 1948 to 1950, and Louisiana State University from 1950 to 1952, when he received the Bachelor of Science degree.

In 1952 he was called to active duty in the United States Army. After his discharge in 1954 he was employed as an engineer by Thiokol Chemical Corporation, Huntsville, Alabama.

He entered graduate school at Louisiana State University in 1955, and is now a candidate for the degree of Doctor of Philosophy.

He is married to the former Inka Fredotovich, of New Orleans, and has a daughter, Tania Mary, nine months old.
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