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Effects of Substitution on the Phosphorescence Process of Aromatic Carbonyl Compounds

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Phosphorescence and absorption spectra, phosphorescence- and excitation-polarization spectra and phosphorescence lifetimes were measured at 77°K for benzaldehyde, acetophenone and their eight derivatives with a halogen atom, or a hydroxyl, methoxyl or amino group as a substituent at the *para* position. In chloro- and bromo-derivatives, the phosphorescent triplet state is of the (n, π^*) type, and is mixed with the ${}^1L_a(\pi, \pi^*)$ state by direct spin-orbit interaction, as in the case of the parent carbonyls. In addition, owing to the heavy-atom effect, it gains its singlet character by the mechanism

$${}^1(\sigma, \pi^*) \text{ or } {}^1(\pi, \sigma^*) \overset{\text{S.O.}}{\longleftrightarrow} {}^3L_a(\pi, \pi^*) \overset{\text{Vib.}}{\longleftrightarrow} {}^3(n, \pi^*)$$

which accounts for the observation that the phosphorescence spectrum involves out-of-plane-polarized vibrational bands. Substitution of a more electron-donating hydroxyl, methoxyl, or amino group brings about a change of the phosphorescent state from the ${}^3(n, \pi^*)$ state to the ${}^3L_a(\pi, \pi^*)$. The following mechanisms are shown to be important to the ${}^3L_a(\pi, \pi^*)$ state:

$${}^1(n, \pi^*) \overset{\text{S. O.}}{\longleftrightarrow} {}^3L_a(\pi, \pi^*)$$

$$\begin{tikzcd}
& {}^1(n, \pi^*) \arrow[dl, leftrightarrow, "\text{Vib.}"'] \arrow[dr, leftrightarrow, "\text{S.O.}"] & \\
{}^1L_a(\pi, \pi^*) & & {}^3L_a(\pi, \pi^*) \\
& {}^3(n, \pi^*) \arrow[ul, leftrightarrow, "\text{S.O.}"] \arrow[ur, leftrightarrow, "\text{Vib.}"'] &
\end{tikzcd}$$

These account for two progressions with mutually perpendicular polarizations observed in the phosphorescence spectrum. The lifetimes for the transitions from the ${}^3L_a(\pi, \pi^*)$ state to the ground state of the substituted carbonyls were found to be substantially shorter than the corresponding lifetimes in aromatic hydrocarbons. This fact is quantitatively interpreted as due to the presence of a low-lying ${}^1(n, \pi^*)$ state.

The radiative process in aromatic carbonyl compounds has been a subject of considerable interest.[1–8] In typical aromatic carbonyls such as benzophenone and acetophenone, the lowest triplet state is of (n, π^*) character, and this fact is believed to lead not only to the characteristic phosphorescence with a short lifetime but also to the high photochemical reactivity of these compounds.[9–11] Perturbation by a suitable substituent or a polar solvent may produce a change in the lowest triplet state from an (n, π^*) to a (π, π^*) type, and this change is expected to be accompanied by an essential change in both the spectral and chemical behaviors of the carbonyl compounds. Studies along these lines have recently been reported.[7–12] In particular, even for weakly perturbed acetophenones like *p*-bromo- and *p*-

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1) S. K. Lower and M. A. El-Sayed, *Chem. Revs.*, **66**, 199 (1966).

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

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4) Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).

5) J. Dehler and F. Dörr, *Tetrahedron Letters*, **1965**, 2155.

6) M. Akagi, Y. Amako and H. Azumi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 689 (1966).

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9) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

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11) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser and R. Dusenbery, *ibid.*, **89**, 5466 (1967).

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methylacetophenone, the lowest triplets were assigned to (π, π^*) states on the basis of S→T absorption spectra obtained by the phosphorescence excitation method.[7,11]

In this study the effects of substitution on the phosphorescence process of aromatic carbonyl compounds have been examined through spectroscopic analysis, polarization and lifetime measurements. Special attention was paid to the polarization of phosphorescence and excitation in relation to the mechanism of spin-orbit coupling. Several *para*-substituted benzaldehydes and acetophenones were investigated. Hydroxyl and amino derivatives display emission characteristics that are definitely ascribable to the lowest triplet state of (π, π^*) type, while the phosphorescent states of halogen derivatives appear to be of (n, π^*) from the results of polarization measurements.

An extensive polarization study was made by Shimada and Goodman[4] on carbonyl compounds including the unsubstituted benzaldehyde and acetophenone.

Experimental

Materials. All the reagents used were obtained from Wako Pure Chemical Industries, Osaka. Benzaldehyde, acetophenone and *p*-chloroacetophenone were purified by vacuum distillation, and *p*-chlorobenzaldehyde, *p*-bromobenzaldehyde and *p*-bromoacetophenone by repeated zone melting. *p*-Hydroxybenzaldehyde, *p*-hydroxyacetophenone and *p*-aminoacetophenone were recrystallized from water and from ethanol, and were further purified by vacuum sublimation. *p*-Methoxybenzaldehyde was fractionally crystallized several times.

Isopentane was refluxed over phosphorus pentoxide, and subjected to fractional distillation. Methylcyclohexane of spectroscopic quality was used without further purification. Ethyl ether was refluxed over metallic sodium, distilled, and was then passed through a freshly activated alumina column.

Apparatus and Procedure. Absorption spectra were obtained with a Hitachi EPS-3 spectrophotometer at 77°K or at room temperature. Emission and excitation spectra and their polarization were measured at 77°K with an apparatus which was constructed in our laboratory.[13] Emission spectra obtained were uncorrected for the spectral sensitivity of the detector. In polarization measurements, monochromatic light, obtained from a combination of 150-W xenon lamp and a grating monochromator (Hitachi G-3), passed through a Frank-Ritter-prism polarizer and irradiated the sample. The light emitted perpendicular to the excitation beam passed through another Frank-Ritter prism as analyzer and a quartz-prism monochromator (Hitachi EPU-2A), and it was then detected by a 1P-28 photomultiplier tube. The polarized spectra were recorded on an X-Y recorder.

The degree of polarization, P, is defined as

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the emitted light polarized respectively parallel and perpendicular to the exciting light which is polarized with the electric vector perpendicular to the plane formed by the excitation beam and the emission beam. The P values were corrected in the usual manner[14] for instrumental and other factors.

All the absorption and emission measurements at 77°K were carried out on rigid-glass samples in a 1-cm square quartz cell placed in a glass Dewar with quartz windows.

Phosphorescence lifetimes were measured using a Becquerel type phosphoroscope combined with a synchroscope.

Results

Figures 1—5 show absorption spectra (A), phosphorescence spectra (P), phosphorescence-polarization spectra (PP) and excitation-polarization spectra (EP) with respect to phosphorescence for benzaldehyde and its derivatives, *p*-chloro-, *p*-bromo-, *p*-hydroxy- and *p*-methoxybenzaldehyde (abbreviated to Cl-, Br-, OH- and OMe-benz-

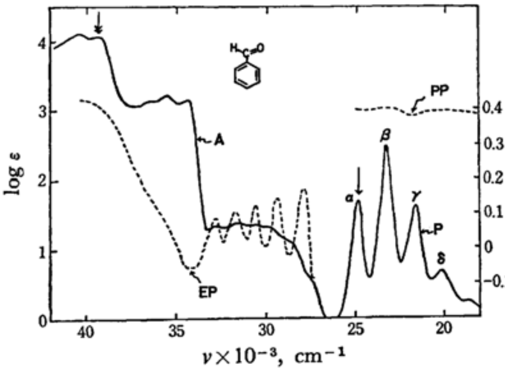

Fig. 1. Absorption, phosphorescence and polarization spectra of benzaldehyde in PME at 77°K.

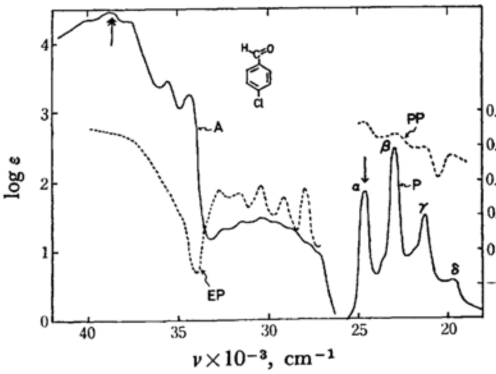

Fig. 2. Absorption, phosphorescence and polarization spectra of *p*-chlorobenzaldehyde in PME at 77°K.

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[13] S. Suzuki, *Bull. Res. Inst. Appl. Elec., Hokkaido Univ.*, **19**, 20 (1967).

[14] T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

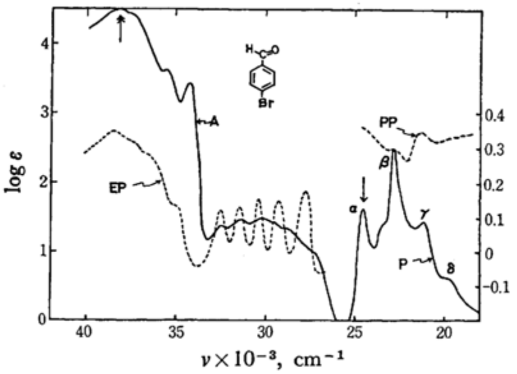

Fig. 3. Absorption, phosphorescence and polarization spectra of *p*-bromobenzaldehyde in PME at 77°K.

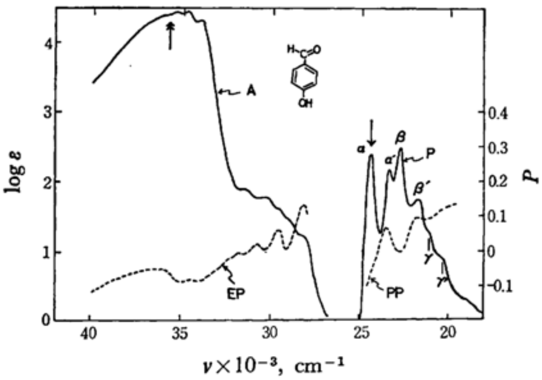

Fig. 4. Absorption, phosphorescence and polarization spectra of *p*-hydroxybenzaldehyde in PME at 77°K.

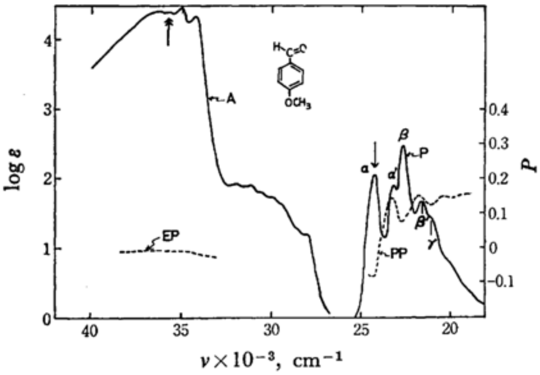

Fig. 5. Absorption, phosphorescence and polarization spectra of *p*-methoxybenzaldehyde in PME at 77°K.

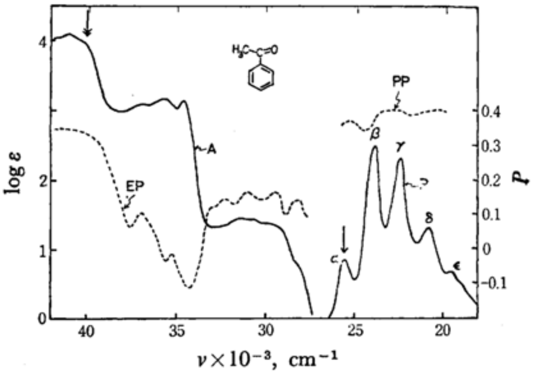

Fig. 6. Absorption, phosphorescence and polarization spectra of acetophenone in PME at 77°K.

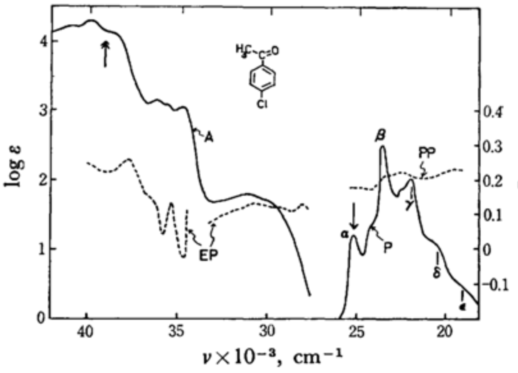

Fig. 7. Absorption, phosphorescence and polarization spectra of *p*-chloroacetophenone in PME at 77°K.

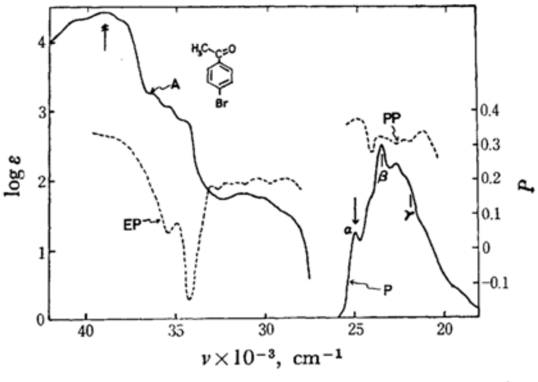

Fig. 8. Absorption, phosphorescence and polarization spectra of *p*-bromoacetophenone in PME at 77°K.

aldehyde, respectively). Similar spectra are shown in Figs. 6—10 for acetophenone and its derivatives, *p*-chloro-, *p*-bromo-, *p*-hydroxy- and *p*-amino-acetophenone (abbreviated to Cl-, Br-, OH- and NH_2-acetophenone, respectively). The excitation and emission frequencies adopted in the polarization measurements are indicated by →→ and →, respectively.

All these spectra were measured at 77°K in an isopentane-methylcyclohexane-ether (PME) mixture (volume ratio, 7.7 : 1.3 : 1). Although it was desirable to use the hydrocarbons alone as the solvent for reducing the solvent perturbation, ether had to be added so that the solute might have the minimum solubility. Nevertheless, no well-

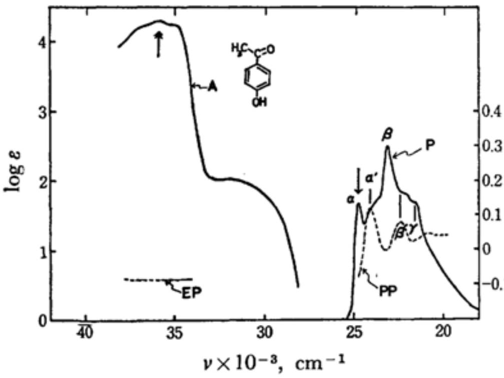

Fig. 9. Absorption, phosphorescence and polarization spectra of *p*-hydroxyacetophenone in PME at 77°K.

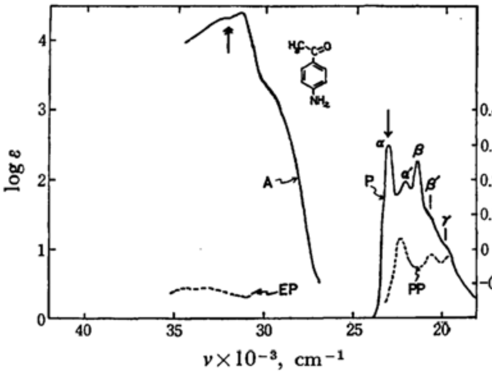

Fig. 10. Absorption, phosphorescence and polarization spectra of *p*-aminoacetophenone in PME at 77°K.

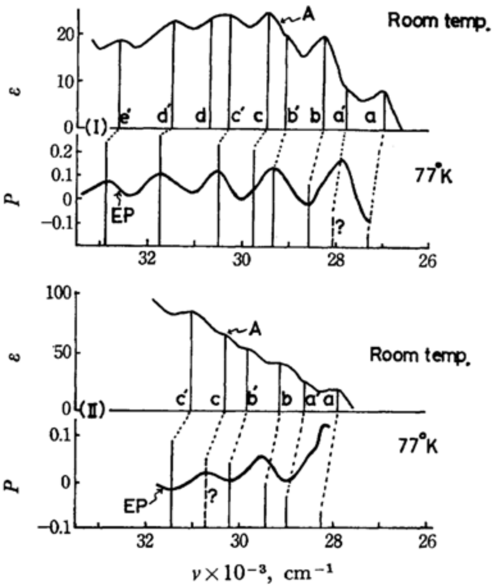

Fig. 11. Excitation-polarization spectra with respect to the phosphorescence 0-0 band in PME at 77°K and absorption spectra in PME at room temperature for benzaldehyde (I) and *p*-hydroxybenzaldehyde (II) in the region of the $n \rightarrow \pi^*$ transition. The location of absorption peaks is shown by vertical lines, the lengths of which represent the molar extinction coefficients, ε. The scale of ε values for the absorption peaks at 77°K is the same as that for the peaks at room temperature.

resolved absorption spectra could be obtained at 77°K in the lowest frequency ($n \rightarrow \pi^*$) region, because of the still low solubility at that temperature. However, the excitation spectra were obtained with a good resolution in the same region.

Detailed spectral data on the excitation polarization in the $n \rightarrow \pi^*$ region for two representative compounds, benzaldehyde and OH-benzaldehyde are shown in Fig. 11, together with the absorption peaks observed at 77°K. For the sake of comparison, the absorption spectra at room temperature are also given in this figure.

TABLE 1. OBSERVED AND CALCULATED PHOSPHORESCENCE LIFETIMES

Compound	τ_{obs} sec	τ_{calc} sec
Benzaldehyde	0.0026	
p-Chlorobenzaldehyde	0.024	
p-Bromobenzaldehyde	0.0070	
p-Hydroxybenzaldehyde	0.14	0.15
p-Methoxybenzaldehyde	0.11	0.13
Acetophenone	0.0043	
p-Chloroacetophenone	0.060	
p-Bromoacetophenone	0.010	
p-Hydroxyacetophenone	0.50	0.28
p-Aminoacetophenone	0.86	0.58

The results of the polarization measurements for benzaldehyde and acetophenone are essentially the same as those reported by Shimada and Goodman,[4] although they employed EPA as the solvent.

The results of the phosphorescence lifetime measurements are recorded in Table 1.

Discussion

Spectral Changes due to Substitution. Benzaldehyde shows three electronic absorption bands in the near ultraviolet region (Fig. 1). The weak absorption band located at 30000 cm⁻¹ is due to an $n \rightarrow \pi^*$ transition, and the other two to $\pi \rightarrow \pi^*$ transitions. The bands at 35000 cm⁻¹ and 40000 cm⁻¹ are assigned respectively to $^1A \rightarrow {}^1L_b$ and $^1A \rightarrow {}^1L_a$ (or an intramolecular charge-transfer) transitions.[4]

The ionization energies of the substituents concerned in this study are in the order $Cl \gtrsim Br > OH \gtrsim OCH_3 > NH_2$.[15] The ^1L_a band is markedly

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[15] F. A. Matsen, "Chemical Applications of Spectroscopy," ed. by W. West, Interscience, New York (1956), p. 673.

shifted to lower frequencies with the decrease of the ionization energy of the substituent (Figs. 2—5). On the other hand, substitution produces no appreciable change in the position of the ^1L_b band, and thus in OH- and OMe-benzaldehyde the latter band is almost hidden under the stronger ^1L_a band. The substitution has no appreciable effect on the position of the $n \rightarrow \pi^*$ band. It may be noted, however, that the $n \rightarrow \pi^*$ band is slightly displaced to the red by chlorine and bromine and to the blue by OH and OMe groups.

The unsubstituted benzladehyde exhibits a phosphorescence spectrum with a well-defined and simple vibrational structure, but the structures of the phosphorescence spectra of the substituted benzaldehydes are more or less complicated.

The foregoing descriptions of the absorption and phosphorescence spectra of benzaldehyde and its derivatives apply on the whole to the spectra of acetophenone and its derivatives (Figs. 6—10).

Polarization. The polarization behaviors of the spectra of the carbonyl compounds studied can be classified into two types, one represented by benzaldehyde and the other by OH-benzaldehyde. Actually, these compounds belong to the symmetry group C_s, but their electronic structure may be discussed in terms of the structure of C_{2v} molecules. The resolution of the representations of C_{2v} into those of C_s is shown in Table 2, the coordinate axes being given in Fig. 12. It should be noted that for the carbonyl compounds concerned the lowest vacant π orbital is of b_1 type,[16] and the n orbital is of b_2 type.

TABLE 2. RESOLUTION OF REPRESENTATIONS

C_{2v}	C_s
$A_1(z)$	$A'(y, z, R_x)$
$A_2(R_z)$	$A''(x, R_y, R_z)$
$B_1(x, R_y)$	$A''(x, R_y, R_z)$
$B_2(y, R_x)$	$A'(y, z, R_x)$

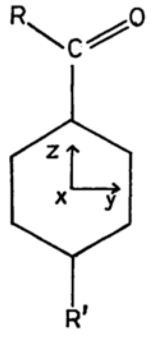

Fig. 12. Structure and coordinate axes for the carbonyl compounds. The x axis is perpendicular to the molecular plane.

The $^1A \rightarrow {^1L_a}$ and $^1A \rightarrow {^1L_b}$ transitions are $^1A_1 \rightarrow {^1A_1}$ and $^1A_1 \rightarrow {^1B_2}$ analogue transitions, respectively. The $n \rightarrow \pi^*$ band is due to a $^1A_1 \rightarrow {^1A_2}$ analogue transition, which is forbidden in the C_{2v} molecules but changes to a symmetry-allowed transition $^1A' \rightarrow {^1A''}$ as a result of the lowering of symmetry from C_{2v} to C_s. Thus, in each of the two representative molecules, benzaldehyde and OH-benzaldehyde, the vibrational progression a, b, c, *etc.* (see Fig. 11) is attributable to the symmetry-allowed transition, with the band a as the 0—0 band. On the other hand, the $n \rightarrow \pi^*$ transition may steal intensity from the $^1A \rightarrow {^1L_a}$ through a vibronic interaction involving an a_2 analogue vibration.[4] This mechanism may account for the second progression a′, b′, c′, *etc.* of the $n \rightarrow \pi^*$ transitions.

To sum up, the $^1A \rightarrow {^1L_a}$ absorption and the a′-progression of the $n \rightarrow \pi^*$ absorption are polarized along the long axis (z) of the molecule and the $^1A \rightarrow {^1L_b}$ is along the short axis (y), while the a-progression of the $n \rightarrow \pi^*$ absorption should be polarized perpendicular to the molecular plane (x axis).[*1]

For benzaldehyde (Figs. 1 and 11), the excitation-polarization spectrum with respect to emission at the phosphorescence 0-0 band, α, is consistent with the view that the phosphorescence 0-0 band is polarized in the molecular plane and along the long axis.[4] The degree of polarization, P, of the phosphorescence with respect to excitation into the $^1A \rightarrow {^1L_a}$ absorption shows highly positive values which are nearly constant throughout the phosphorescence spectrum. This implies that the phosphorescence spectrum of benzaldehyde consists almost of a single progression, α, β, *etc.*, with the 0—0 band α as its first member.

The excitation-polarization spectra of Cl- and Br-benzaldehyde are essentially the same as that of benzaldehyde. Thus the phosphorescence 0-0 band, α, of the halo-derivatives must be polarized along the long axis. On the other hand, the phosphorescence-polarization spectra of these derivatives show distinct variations in the P value. This fact together with the features of their phosphorescence spectra suggests that the phosphorescence spectra involve a progression which differs in polarization from the main progression including the 0-0 band.

The excitation- and phosphorescence-polarization spectra of acetophenone and its chloro- and bromo-derivatives are on the whole similar to the corresponding spectra of benzaldehyde and its chloro- and bromo-derivatives, respectively. Therefore, the preceding discussions on the latter molecules are applicable to the former as well. It is to be noted, however, that in acetophenone the phosphorescence-polarization spectrum shows an

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[16] K. Inuzuka and T. Yokota, This Bulletin, **37**, 1224 (1964).

[*1] The progressions starting from the bands a and a′ are called a- progression and a′-progression, respectively.

appreciable variation in the P value, which is not found in the case of benzaldehyde.

The situation is radically changed on going from benzaldehyde to OH-benzaldehyde. Thus, with respect to emission at the phosphorescence 0–0 band, α, the excitation-polarization spectrum of OH-benzaldehyde shows negative P values in the region of the $^1A \rightarrow {}^1L_a$ band and minimum values of P at the vibrational peaks of the a′-progression, whereas the P values are positive at the peaks of a-progression (Figs. 4 and 11). Further, the P values appear to be negative in the region of $^1A_1 \rightarrow {}^1L_b$ absorption, which is not clearly separated from the $^1A_1 \rightarrow {}^1L_a$ absorption. These observations lead to the conclusion that the phosphorescence 0–0 band α is polarized perpendicular to the molecular plane.

Inspection of the phosphorescence and phosphorescence-polarization spectra of OH-benzaldehyde shows that, in addition to the out-of-plane-polarized α-progression, there is an inplane-polarized progression, α', β', *etc.*, which is polarized along the long axis. The spacing between successive bands of each of the α- and α'- progressions is about 1550 cm^{-1}. The origin (band α') of the latter progression is situated about 900 cm^{-1} from the 0–0 band to the red.

The polarization characteristics and spectral features of OCH_3-benzaldehyde, and OH- and NH_2-acetophenone (Figs. 5, 9 and 10) are similar to those of OH-benzaldehyde mentioned above.

Mechanisms of Spin-Orbit Coupling and Assignment of the Phosphorescent States. The polarization data may be explained by considering the mechanisms of spin-orbit coupling in the carbonyl compounds. The following discussions are based on a few assumptions.[1] (1) The perturbation of the ground state by triplet states is negligible. (2) The first-order spin-vibronic perturbation is negligible. (3) The spin-orbit operator, H_{SO}, can be approximated as a sum of one-electron operators. According to these assumptions, spin-orbit coupling through H_{SO} occurs only between electronic states resulting from one-electron excitations which take place either from the same occupied molecular orbital or to the same vacant orbital. The phosphorescent state of benzaldehyde can be assigned to the $^3A_2(n, \pi^*)$ analogue,[4] which couples directly with the $^1A_1\ (\pi, \pi^*)$ state through the first order spin-orbit perturbation, $H_{SO}(R_z)$. We can write as

$$^1L_a(\pi, \pi^*) \overset{\text{S.O.}}{\longleftrightarrow} {}^3(n, \pi^*) \qquad (1)$$

The above mechanism accounts for the polarization features in the compounds of the benzaldehyde type, namely, the long-axis polarization of the α-progression, including the 0–0 band, of the phosphorescence spectra. The effective spin-orbit perturbation of the first order along with the high intensity of the $^1A \rightarrow {}^1L_a$ transition should result in very short phosphorescence lifetimes for these compounds. This is indeed the case, as seen in Table 1.

The aromatic carbonyl compounds are considered to have the $^3L_a(\pi, \pi^*)$ state close to the $^3(n, \pi^*)$ state. Because of the small energy difference between the two triplet states, an effective vibronic interaction involving an a_2 analogue vibration is expected to occur, so that the $^3(n, \pi^*)$ state will be mixed with singlet states through the second-order spin-orbit-vibronic perturbation. In most aromatic hydrocarbons, $^3(\pi, \pi^*)$ states are known to gain their singlet characters by direct coupling with $^1(\sigma, \pi^*)$ or $^1(\pi, \sigma^*)$ states.[1] Thus, in addition to mechanism (1), the following may also be responsible for the transition $^3(n, \pi^*) \rightarrow S_0$ (ground state):

$$^1(\sigma, \pi^*) \text{ or } {}^1(\pi, \sigma^*) \overset{\text{S.O.}}{\longleftrightarrow} {}^3L_a(\pi, \pi^*) \overset{\text{Vib.}}{\longleftrightarrow} {}^3(n, \pi^*) \qquad (2)$$

In the absence of a heavy atom, mechanism (2) is negligible as compared with mechanism (1). When the molecule contains a heavy atom, the spin-orbit interaction between ^3L_a and $^1(\sigma, \pi^*)$ or $^1(\pi, \sigma^*)$ will be enhanced to increase the relative importance of mechanism (2).[17] Accordingly, the $^3(n, \pi^*) \rightarrow S_0$ transition will be provided with an out-of-plane transition moment.

In the chloro- and bromo-derivatives of benzaldehyde, the phosphorescence-polarization spectra show variations in the P values; there appear minima in the positive P curves. Furthermore, the vibrational structures of the phosphorescence spectra of the halo-derivatives are more or less irregular. These observations can reasonably be explained in terms of mechanism (2).

By following the same reasoning, we can interpret the phosphorescence and phosphorescence-polarization spectra of the chloro- and bromo-derivatives of acetophenone. If this interpretation is correct, however, one problem will remain unsolved. That is, as has been pointed out, the phosphorescence-polarization spectrum of the unsubstituted acetophenone exhibits a variation. This cannot be attributed to mechanism (2), since the acetophenone molecule has no heavy atom. On the other hand, the phosphorescence spectrum itself is fairly simple as in the case of benzaldehyde. This fact suggests that the out-of-plane component should be negligible in the phosphorescence polarization of acetophenone. In any case, further studies are necessary for understanding fully the polarization behavior of the phosphorescence of acetophenone.

The radical changes in polarization produced by substitution of OH, OCH_3 and NH_2 groups can be best understood by taking account of possible

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[17] M. A. El-Sayed, *J. Chem. Phys.*, **43**, 2864 (1965).

changes in the phosphorescent state. Substitution of such electron-donating groups leads to a considerable lowering of the energy level of the ^1L_a state and to a slight rise of the $^1(n, \pi^*)$ level. If the ^3L_a and $^3(n, \pi^*)$ states behave similarly, the positions of the ^3L_a and $^3(n, \pi^*)$ levels are expected to be reversed, with the result that the ^3L_a state is the lowest triplet in the compounds of the OH-benzaldehyde type.

The mechanisms of the spin-orbit coupling in these molecules were examined on the assumptions mentioned before and also on the premise that the direct spin-orbit coupling between $^1(\pi, \pi^*)$ and $^3(\pi, \pi^*)$ states is vanishingly small.[1] Of the several possible mechanisms the following two seem to be most important:

$$^1(n, \pi^*) \overset{\text{S.O.}}{\longleftrightarrow} {}^3L_a(\pi, \pi^*) \tag{3}$$

$$\begin{tikzcd}
 & {}^1(n, \pi^*) \arrow[dl, leftrightarrow, "\text{Vib.}"'] \arrow[dr, leftrightarrow, "\text{S.O.}"] & \\
{}^1L_a(\pi, \pi^*) \arrow[dr, leftrightarrow, "\text{S.O.}"'] & & {}^3L_a(\pi, \pi^*) \\
 & {}^3(n, \pi^*) \arrow[ur, leftrightarrow, "\text{Vib.}"'] &
\end{tikzcd} \tag{4}$$

As will be seen later, the lifetime data show that the coupling mechanism which is important for the phosphorescent $^3(\pi, \pi^*)$ state of aromatic hydrocarbons is not operative in the carbonyl compounds in question. Thus, the direct spin-orbit interaction between $^3L_a(\pi, \pi^*)$ and $^1(\sigma, \pi^*)$ or $^1(\pi, \sigma^*)$ is not considered here.

As regards mechanism (3), the transition between the ground state and the perturbing singlet, $^1(n, \pi^*)$, is forbidden in the C_{2v} molecules, but it becomes symmetry allowed in the actual C_s molecules. On the other hand, a large absolute value is anticipated for the matrix element of H_{SO} between the $^1(n, \pi^*)$ and ^3L_a states. Thus, the mechanism (3) plays a major role in the phosphorescence transition, and it accounts for the out-of-plane polarization of the α-progression that includes the 0–0 band.

Mechanism (4) involves second-order interactions. Its importance is considered to be comparable with the importance of mechanism (3), since in the singlet $n \rightarrow \pi^*$ absorption the intensities of the a- and a′-progressions are of comparable magnitudes. Mechanism (4) results in the appearance of the α'-progression which is vibronically induced and is polarized along the long molecular axis.

Mention should be made here of the assignment of the triplet states which was made by Kearns and Case on the basis of singlet→triplet absorption spectra.[7] According to their results, the lowest triplet state is a $^3(n, \pi^*)$ state for benzaldehyde, Br-benzaldehyde and acetophenone, and is a $^3(\pi, \pi^*)$ state for OH-acetophenone, in agreement with the present assignment. As to Br-acetophenone, they assigned the lowest triplet state as a $^3(\pi, \pi^*)$ state, whereas we regard it as a $^3(n, \pi^*)$. Our assignment is based on the observation that the phosphorescence 0–0 band of Br-acetophenone is highly positively polarized with respect to excitation into the $^1A \rightarrow {}^1L_a$ absorption band. Inspection of Figs. 3 and 8 will show that there is no substantial difference in the polarization spectra between Br-benzaldehyde and Br-acetophenone, so that the latter compound should have the same type of phosphorescent state as the former, *viz.*, an (n, π^*) type of phosphorescent state. It should be noted that the discrepancy between the two assignments might result from the difference between the samples employed. (Kearns and Case used a crystalline sample of Br-acetophenone doped with naphthalene.)

Lifetimes. As seen in Table 1, the molecules with the phosphorescent triplet state of (π, π^*) type have relatively long lifetimes. However, they are still markedly shorter than the lifetimes of the $^3(\pi, \pi^*) \rightarrow S_0$ phosphorescence emissions in aromatic hydrocarbons. This problem has recently been noticed by several authors[7,12,18,19] in aromatic azines and carbonyls, and has been discussed from the viewpoint of participation of a low-lying $^1(n, \pi^*)$ state in the spin-orbit coupling.

The matrix element

$$\langle {}^1(n, \pi^*) | H_{SO} | {}^3L_a(\pi, \pi^*) \rangle \tag{5}$$

which is associated with mechanisms (3) and (4) can be equated to

$$\langle {}^1L_a(\pi, \pi^*) | H_{SO} | {}^3(n, \pi^*) \rangle \tag{6}$$

provided that $^1(n, \pi^*)$ and $^3(n, \pi^*)$ have the same spatial configuration.[20]

In a previous paper,[12] we assumed the matrix element (6) of OH-benzaldehyde to be approximately equal to the corresponding element for the unsubstituted benzaldehyde (*cf.* mechanism (1)), and thus calculated the phosphorescence lifetime of OH-benzaldehyde. Similar calculations were made for molecules whose phosphorescent states have been assigned to the $^3(\pi, \pi^*)$ states in this study. The calculated lifetimes, τ_{calc}, which correspond to the observed lifetimes (rather than to the natural lifetimes) were obtained by assuming that the substitution leads to no change in the phosphorescence quantum yield. This assumption is based on the observation that the phosphorescence intensity was not appreciably changed by substitution. The results are shown in Table 1. In spite of the assumptions involved, the τ_{calc} values are in good agreement with the τ_{obs} values.

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