List of Publications


8. $^3n^\pi^*$ assignment of the lowest triplet state of p-methyl acetophenone – S. K. Ghoshal, and G. S. Kastha, Chem. Phys. Lett. (communicated)


Effects of Intermolecular Hydrogen-bonding on the Luminescence Properties of Acetophenone. Characterization of Emission States

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The effects of intermolecular hydrogen-bond formation by protic solvents on the absorption and luminescence properties of acetophenone have been investigated. It has been concluded from analysis of the T$\rightarrow$S$_0$ absorption, phosphorescence excitation spectra and the emission characteristics that the lowest triplet state of acetophenone in its vapor phase and in nonpolar as well as in moderately polar solvents (e.g., ethanol, EPA etc.) is of n-\pi* character. In rigid polar media, acetophenone exhibits a very weak \( \pi-\pi^* \rightarrow S_0 \) fluorescence and a weak \( n-\pi^* \rightarrow S_0 \) phosphorescence superposed with the principal \( n-\pi^* \rightarrow S_0 \) emission. A progressive enhancement of both of these emissions with increasing polarity of the solvent has been observed. It is shown that the fluorescence and the dual phosphorescence emissions from acetophenone in rigid polar media arise as a result of decreased efficiencies of the spin-orbit and vibronic coupling interactions due to intermolecular hydrogen-bond formation by the protic solvents.

In spite of extensive spectroscopic$^{1-13}$ and photophysical$^{14-21}$ studies ambiguity remains concerning the assignment of the lowest triplet state of acetophenone. The phosphorescent state of acetophenone in glassy nonpolar and moderately polar media (e.g., ethanol, EPA) at 77 K has been shown to possess a n-\pi* character by several investigators$^{1-10}$ and a \( \pi-\pi^* \) character by others.$^{7,9}$ More recently, Mathews and Lytle$^9$ characterized it as n-\pi* and \( \pi-\pi^* \) type in polar (ethanol, methanol) and nonpolar media, respectively, at 77 K. In the case of pure acetophenone crystal, \( \pi-\pi^* \) assignment was made of its lowest triplet state on the basis of polarized phosphorescence-excitation spectra$^{11}$ and PMDR studies$^{18}$ and n-\pi* assignment on the basis of T$\rightarrow$S$_0$ absorption$^{16}$ and the polarization and Zeeman splitting measurement of the T$\rightarrow$S$_0$ absorption.$^{17}$

As regards the origin of dual phosphorescence emissions in rigid polar media, the phenomenon has been interpreted on the basis of various assumptions.$^{14,17}$ Koyanagi et al.$^5$ proposed a model of highly distorted (triple minimum) potential surface in the lowest triplet state of acetophenone in order to explain its dual phosphorescence. A non-interacting density of states model has been postulated to account for the phenomenon. In each case a close proximity of the n-\pi* states has been assumed as an essential prerequisite for the occurrence of dual phosphorescence emission, but little information is given on the relative positions of the triplet levels in environments pertinent to the problem. The dual phosphorescence is observed in rigid polar media and H-bond acceptor properties of the aromatic ketone$^{5,12,20}$ but the possibility that this phenomenon could be associated with the solute-solvent intermolecular H-bonding interaction has not been considered.

Though the fluorescence activation of several aromatic aldehydes, ketones and other carbonyl compounds in protic media is well known$^8$ no investigation seems to have been made on the possibility of fluorescence activation in the case of acetophenone.

In view of the significance of luminescence properties of aromatic carbonyls in hydrogen bonding media and the conflicting assignment of the lowest triplet state of acetophenone, a detailed investigation on the absorption and emission characteristics of this aromatic ketone has been carried out. This study was carried out in order to obtain information on the relative positions of the n-\pi* and \( \pi-\pi^* \) levels of acetophenone under various conditions, and to examine the effect of intermolecular H-bonding on the photophysical behavior of this phenyl alkyl ketone.

**Experimental**

Materials. Acetophenone (ECA-Chemic, West Germany) was purified by repeated fractional distillation till no impurity could be detected with a flame ionization detector column (Hewlett-Packard, Model 5730A). Spectrograde ethanol, ether, isopentane, and 3-methylpentane (3-MP) of E. Merck and hexane, pentane, and methylcyclohexane of BDH were further purified by fractional distillation.

Apparatus: The room temperature (300 K) solution and vapor phase (ca. 10$^{-4}$ Torr) emission spectra and low temperature (77 K) emission, excitation and polarization spectra were recorded on a Perkin Elmer Model MFP 44A fluorescence spectrophotometer. The vapor phase absorption spectra with 10 cm quartz cell at 300 K and 760 Torr and the solution spectra at 300 K and 77 K with a 1 cm quartz cell were obtained with a Shimadzu 210A UV-VIS Absorption spectrophotometer. Photoelectron technique was employed for the measurement of the degree of polarization, which was corrected following Azumi and McGlynn.$^{23}$ The phosphorescence lifetimes were determined by using Molecotron UV-1000 N$_2$-Laser as the excitation source in conjunction with an EG storage Oscilloscope.

**Results**

**Absorption Characteristics.** Figure 1 shows the absorption spectrum of acetophenone in the vapor phase and in protic as well as aprotic solvents at room temperature (300 K). Appreciable solvatochromic effects, such as the hypso- and bathochromic shifts, respectively, of 1 Torr=133.322 Pa.

of aqueous solution of peroxomonosulfate.


Novel luminescence properties of acetophenone in hydrogen-bonding media are presented, focusing on singlet-singlet absorption and phosphorescence excitation spectra.

**Figure 1.** Singlet-singlet absorption spectra of acetophenone in the vapor phase (---), 3-MP (--), and 1% HCl (-----) at 300 K.

**Figure 2.** Phosphorescence excitation spectra of acetophenone in 3-MP (------) and ethanol (---) at 77 K.

*Table 1.* Relative positions (cm$^{-1}$) of the n-π* and π-π* singlet and triplet states of acetophenone measured from the absorption spectra$^a$.

<table>
<thead>
<tr>
<th>Electronic energy levels</th>
<th>300 K</th>
<th>77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vapor</td>
<td>3-MP</td>
</tr>
<tr>
<td>$\pi_{n}$</td>
<td>42092</td>
<td>41925</td>
</tr>
<tr>
<td>$\pi_{n}$</td>
<td>35387</td>
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<td>$\pi_{n}$*</td>
<td>27886</td>
<td>26617</td>
</tr>
<tr>
<td>$\pi_{n}$*</td>
<td>26517</td>
<td>26717</td>
</tr>
<tr>
<td>$\pi_{n}$*</td>
<td>25899</td>
<td>26000</td>
</tr>
</tbody>
</table>

$^a$ Values in parentheses are obtained from the phosphorescence excitation spectra at 77 K. b) Data in ethanol-water mixture.

The phosphorescence excitation spectra of acetophenone in 3-MP and ethanol show a significant lowering (ca. 100 cm$^{-1}$) of the excited state carbonyl stretching frequency of the molecule in ethanol as compared to that in 3-MP glass (Table 2). With increase in the polarity of the medium (e.g., from ethanol to predominantly ethanol-water mixture), further obliteration of the n-π*-S$_0$ bands takes place. In highly polar and acidic media (1% HCl), these bands are no longer observable in the phosphorescence excitation spectra. The $\pi_{n}$ bands also show a similar solvent dependent intensity variation.

Both the vapor and solution phase T-S$_0$ absorption spectra of acetophenone (Fig. 3) display two weak but distinct bands. The spectral positions of these bands under different environmental conditions are given in Table 1. From a consideration of the relative changes in absorbance and the solvatochromic shifts exhibited by the bands on passing from the vapor phase to hydrocarbon and to polar solvents, the respective assignments of these bands to $\pi-\pi^*$ and $\pi-\pi^*$ transitions have been made (Fig. 3). The bands can be clearly discerned in the phosphorescence excitation spectra of acetophenone in polar as well as in nonpolar media at 77 K (Fig. 2). In glassy hydrocarbon (3-MP), the lower energy band (25833 cm$^{-1}$) has an eminent overlap with the phosphorescence band origin (25815 cm$^{-1}$), the higher energy one appearing at 26833 cm$^{-1}$, i.e., 450 cm$^{-1}$ towards the higher frequency side of the former. The assignment of these bands to $\pi-\pi^*$ and $\pi-\pi^*$, respectively, on the basis of their characteristic solvatochromic shifts and hypochromic effects are analogous to and conform with those made in the case of absorption.

**Emission Characteristics.**

**a) Phosphorescence Spectra:** Figure 4 shows the phosphorescence and the phosphorescence polarization (PP) spectra of acetophenone in glassy polar, EPA (ether, isopentane, and ethanol) media.
Table 2. Observed values of phosphorescence band origin, fundamental frequencies, mean phosphorescence lifetime ($\tau_p$) and quantum yield ratio ($\Phi_p/\Phi_F$) of acetophenone

<table>
<thead>
<tr>
<th></th>
<th>300 K</th>
<th>77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vapor</td>
<td>Isopentane</td>
</tr>
<tr>
<td>Phosphorescence band origin/cm$^{-1}$</td>
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</tr>
<tr>
<td>Fundamental frequency/cm$^{-1}$</td>
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<td>1709</td>
</tr>
<tr>
<td>$\tau_p$/ms</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>$\Phi_p/\Phi_F$</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Ref. 6. b) Lifetime in acidic media. c) Value in ethanol-water mixture. d) Value in 1% HCl. * C=O stretching frequencies obtained from $^{1}n$-$\pi^{*}$-S$\pi$ phosphorescence excitation spectra at 77 K. $\Phi_p/\Phi_F$ values are considered to be qualitative.

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Fig. 3. Singlet-Triplet absorption spectra of acetophenone (a) in the vapor phase (-----), 3-MP (----) and ethanol (------) at 300 K. (b) In 3-MP (----) and ethanol (------) at 77 K.

Fig. 4. Phosphorescence (P) and phosphorescence polarization (PP) spectra (with 250 nm excitation) of acetophenone in 3-MP (-----) and EPA (-----) at 77 K.

5:5:2) and nonpolar (3-MP) media under identical conditions. Despite the close resemblance of the two spectra, distinct changes in phosphorescence spectra brought about by the protic solvent are apparent:

1. The sharp and structured phosphorescence spectrum observed in 3-MP at 77 K appears broadened in EPA glass.
2. A substantial blue shift (ca. 190 cm$^{-1}$) of the phosphorescence band origin and lowering of carbonyl stretching frequency ($\nu_{C=O}$) occurs with the change of solvent from nonpolar to polar.
3. A significant diminution in phosphorescence intensity of acetophenone takes place in polar media in comparison with that in glassy hydrocarbon matrices.
4. Whereas the phosphorescence intensity on the smaller wavelength side of the 0-0 band in glassy hydrocarbon matrices falls steeply, in glassy polar media the band origin is accompanied by a short tail which extends to the higher frequency region beyond the band maximum (384.5 nm). In fact, the phosphorescence spectrum of acetophenone recorded with an expanded scale and higher resolution (Fig. 5) reveals a weak partially resolved blue shoulder at ca. 381 nm.

The phosphorescence polarization (PP) curves of acetophenone in glassy hydrocarbon (3-MP) and polar (EPA) media show that in both cases the phosphorescence is strongly positively polarized with respect to $^{1}n$-$\pi^{*}$ excitation, indicating a predominantly in-plane polarization of the phosphorescence emission (Fig. 4). The sharp fall in the value of the degree of polarization ($P$) in the 3-MP curve around the immediate vicinity of the phosphorescence band origin indicates the presence of some low frequency nontotally symmetric vibronic band in the phosphorescence spectrum. An important distinction between the PP curves in 3-MP
and EPA glass is that the $P$ value is predominantly more positive in aprotic medium than in protic medium. The PP curve in EPA also shows markedly less positive value at 381 nm. A further decrement of the polarization is observed in more polar EWA (ether, water, and ethanol 5:1:4) glass at 77 K.

The phosphorescence decay curves for acetophenone show that while the nature of the decay is nearly exponential in the case of vapor and in hydrocarbon solutions, it is markedly nonexponential (in fact, biexponential) in rigid polar media like ethanol and water at 77 K (Fig. 6). The initial and final slopes of a first order plot from the decay curves of acetophenone in ethanol glass correspond to lifetimes ($\tau_p$) of ca. 5 and 70 ms, respectively. The shorter lived component of the phosphorescence emission is, however, found to be contributing mostly (ca. 90% of the total intensity) to the phosphorescence intensity. In ethanol–water mixture at 77 K the $\tau_p$ values corresponding to the short and long lived components are 6 and 100 ms, respectively, in agreement with the earlier findings.

As the polarity of the solvent is increased there occurs an enhancement in the intensity of the longer lived component of the dual phosphorescence emission until in strongly acidic media it overwhelms the shorter lived one. In this case the phosphorescence lifetime becomes of the order of seconds. This result is similar to that reported by Lamola.

Thus, the predominantly in-plane polarization of the phosphorescence emission, the short lifetime, the solvent shifts and the vibronic structure of the phosphorescence emission provide the conclusive evidence for the n-$\pi^*$ character of the lowest triplet state of acetophenone in its vapor phase and in nonpolar as well as moderately polar media (e.g., EPA, ethanol) at 77 K. The T-S$_0$ absorption spectra of the compound strongly confirm the n-$\pi^*$ nature of its lowest triplet state in these media.

**b) Fluorescence Spectra:** In addition to its characteristic strong $^3\!\!\!\!n\!-\!\pi^*\rightarrow$S$_0$ phosphorescence emission, acetophenone in rigid protic media at 77 K exhibits a very weak $^1\!\!\!\!n\!-\!\pi^*\rightarrow$S$_0$ fluorescence with $L_0$ and $1L_n$ excitation (Fig. 7). Increase in the polarity or H-bond forming capacity (e.g., ethanol–water, 1% HCl) of the media results in a progressive enhancement of such fluorescence but a gradual decrease in the phosphorescence intensity in the same order. The measured $\Phi_p/\Phi_f$ values of acetophenone in these polar media are given in Table 2. The data when combined with the reported value of $\Phi_p(=0.6)$ for acetophenone yield an approximate $\phi_f$ value of $1.2 \times 10^{-3}$ for this molecule in ethanol. Under these conditions, no emission attributable to the $^1\!\!\!\!n\!-\!\pi^*\rightarrow$S$_0$ fluorescence could be detected.

**Discussion**

Occurrence of the phenomena, viz., blue-shifts of the n-$\pi^*$ bands, hypochromic effect on the n-$\pi^*$ and $\pi\!-\!\pi^*$ ($1L_n$) bands, significant lowering of $\nu_{00}$ fluorescence activation and dual phosphorescence emission from acetophenone in protic media and the progressive enhancement of each with increasing solvent H-bond

![Graph](image-url)
intermolecular H-bonding capacity, indicates a close interrelation with intermolecular H-bonding. It might be related to changes in the electronic configuration of the aceto- phenone molecules caused by solute-solvent interaction, in view of the importance of the electronic structure associated with the carbonyl group, particularly the nonbonding (n) orbital on the oxygen atom, in determining the photophysical behavior of the aromatic ketones and the possible involvement of the oxygen electrons in intermolecular H-bond formation.

The hypsochromic shift of \( \pi^* \rightarrow n \) transition bands of carbonyls in H-bonding media has now been established. It is known by infrared and Raman studies that the \( v_{\text{O}} \) of carbonyls decreases with increasing H-bonding. Our experimental results are in line with these findings.

Intermolecular H-bonding interaction between the proton acceptor carbonyls and the donor protic molecules affects the electronic configuration of the carbonyl group in several ways. It increases the polarity of the carbonyl group (in the direction C=O) by increasing the \( n \) electron charge on the carbonyl oxygen atom. As a consequence, the C-O bond strength decreases leading to an increased C-O bond length and smaller \( v_{\text{O}} \). Since the \( n \) electrons on the carbonyl are primarily involved in intermolecular H-bond formation, such solute-solvent interaction is expected to have a pronounced effect on the \( n \) orbital of the oxygen atom. The work of Hollas et al. indicates that the \( s \) character of the \( n \) orbital and its extent of delocalization are important in determining the \( \pi^* \rightarrow n \) transition intensity in aromatic aldehydes and ketones. The marked diminution in the intensity of \( n^* \) bands of aceto- phenone observed in going from hydrocarbon to hydroxyl solvents suggests an appreciable decrease in the \( s \) character of the \( sp^2 \) hybridized \( n \) orbital of the carbonyl oxygen atom.

In aromatic aldehydes and ketones, because of the presence of closely spaced \( n^* \) and \( \pi^* \) electronic states (the \( n^* \) states being the lower-lying one), the spin-orbit and vibronic interactions between \( n^* \) and \( \pi^* \) excited states are generally very strong. The radiationless deactivation processes, such as internal conversion (IC) and intersystem crossing (ISC) between the pertinent excited states, are very fast and efficient in these types of molecules. This largely accounts for their nonfluorescent nature. The occurrence of \( n^* \) fluorescence from aceto- phenone in protic media and the progressive enhancement of such emission with increasing H-bond donor capacity of the solvent thus imply a considerable decrease in the efficiency of ISC or IC, or of both in such media.

The rate or the efficiency of IC between the \( n^* \) and \( \pi^* \) states is dependent to a significant extent on the vibrational overlap integral between the states concerned. Since the magnitude of vibrational overlap integral between \( n^* \) and \( \pi^* \) states decreases as a result of decrease in the charge density of the nonbonding electrons following H-bond formation, it is expected that the efficiency of IC between the \( 1^\pi \) and \( 3n^* \) states of aceto-phenone would decrease in protic media.

The magnitude of spin-orbit coupling between the \( n^* \) and \( \pi^* \) states of aromatic aldehydes and ketones molecules is largely governed by factors such as the partial \( \pi \) electron density (C1) and Slater charge \( (Z_q) \) on the carbonyl oxygen atom and the form (hybridization and extent of delocalization) of the \( n \) orbital on this atom. It follows that while the \( \pi \) electron density on the carbonyl oxygen atom increases a little, the hybridization factor \( (\gamma) \) undergoes a significant decrement upon H-bond formation. The analysis of Del Bene shows that the increase of \( \pi \) electron charge on the heteroatom due to H-bonding leads to the lowering of the effective nuclear charge \( (Z_q) \) of the atom. Because of the dependence of the spin-orbit interaction matrix element, \( |\beta|^2 \) (Eq. 8, Ref. 36), on the higher power of \( Z \) and the fact that both \( \gamma \) and \( Z \) values decrease as a result of H-bonding, it seems that there is an overall decrease in the value of \( |\beta|^2 \), despite a small increment in the value of C1. Accordingly, the spin-orbit coupling between the \( n^* \) and \( \pi^* \) states of aceto-phenone should decrease in H-bonding media, and so should the ISC rate between them. It is conceivable, therefore, that because of the decreased efficiencies or rates of \( n^* \rightarrow \pi^* \) IG and \( n^* \rightarrow \pi^* \) ISC, the \( n^* \rightarrow \pi^* \rightarrow S_\alpha \) radiative process may become to some extent competitive with these radiationless processes such that some \( n^* \) fluorescence could be emitted from aceto-phenone molecules in protic media.

The \( \lambda_L \) state of aromatic aldehydes and ketones (e.g., benzaldehyde and aceto-phenone) which provides the dipole allowed character and in-plane polarization to the lowest triplet state through spin-orbit coupling is known to possess considerable intramolecular charge transfer character. The marked diminution in the \( \lambda_L \) band intensity of aceto-phenone in protic media indicates that the intramolecular charge transfer character of the associated singlet-singlet \( \pi^* \rightarrow \pi^* \) transition is perhaps inhibited as a result of solute-solvent H-bonding interaction. The significant lowering of the P values of phosphorescence emission from aceto-phenone molecules in H-bonding media, compared to those observed in nonhydrogen bonding media, could be related, at least partly, to the diminished spin-orbit coupling between \( \pi^* \rightarrow \pi^* \) (\( \lambda_L \)) and \( n^* \) state due to H-bonding. This may be interpreted as evidence in favor of the supposition that the spin-orbit coupling should decrease in H-bonding media.

The simultaneous emission of phosphorescence from both the triplet states (\( n^* \) and \( \pi^* \)) of aceto-phenone in protic media suggests that the solvent induced decrease in the efficiency of \( n^* \rightarrow \pi^* \rightarrow S_\alpha \) IC process could be at the basis of such phenomenon.

According to Avouris et al., the rate constant of the IC process between two states is given by

\[
K_{\text{IC}} = 2\pi|V_{\text{IC}}|^2, \tag{1}
\]

where \( p(E) \) is the density of closely spaced state \( |\psi\rangle \) (final) nearly degenerate with the initial state \( |\psi_i\rangle \) and \( V_{\text{IC}} \) is the interaction matrix element for the IC process. \( |V_{\text{IC}}|^2 \) is dependent on the electronic factor \(|\beta|^2 \) and vibrational overlap integral.

Intermolecular H-bonding can bring about a dimi-
Luminescence Properties of Acetophenone in Hydrogen-bonding Media

...the overlap integral through the decrease of nonbonding charge density. It can be shown that the magnitude of $V_{\text{eff}}$ in the triplet manifold would also decrease as a result of intermolecular H-bond formation. We see from Eq. 1 that the density of states, $\rho(E)$ could also be an important factor contributing to the radiationless transition between the two triplet states. Because of the smaller energy gap between the $T_2 (\pi-\pi^*)$ and $T_1 (n-n^*)$ states of acetophenone in protic solvents, the level densities of $T_1$ near the $T_0$ origin are expected to be small. Consequently, internal conversion from the low-lying vibrational levels of $T_2$ to $T_1$ would be less efficient. As a result of the combined effect of a decrease in both these factors, it is possible that the $T_2 \rightarrow n\rightarrow T_1$ IC rate would become sufficiently slow so as to make the $n-\pi^* \rightarrow \pi^*$ radiative process to some extent competent with the IC process, leading to the observation of phosphorescence emission. Several authors previously observed dual phosphorescence emission from other aromatic ketones, e.g., 2-benzoxquinone, indanone, and related molecules in rigid polar media, and attributed the phenomenon to severely prohibited internal conversion from the $n-\pi^*$ state to a lower lying $n-\pi^*$ state of these molecules.

Thus, the profound influence of the H-bonding solvents on the luminescence spectral properties of acetophenone is seen to arise primarily from the electronic effect of the intermolecular H-bonding interaction. When polarity or H-bond donor capacity of the solvent increases, the ISC and IC processes become progressively less efficient and a trend of progressive enhancement of the $n-\pi^*$ fluorescence and $n-\pi^* \rightarrow \pi^*$ phosphorescence is observed. In strongly acidic media protonation of the carbonyl lone pair electrons occurs; the conjugation of the oxygen electrons across the carbonyl group and the intramolecular charge transfer character of the $T_1 (\pi^* \rightarrow n)$ transition are strongly affected. In this situation, as the $n$ electrons on the carbonyl oxygen atom no longer remain nonbonding, the $\pi^*-n$ electronic transition loses its significance and the luminescence characteristics exhibited by the protonated species become more or less normal $\pi-\pi^*$ type.

References

Circular Dichroism of Chromium(III) Complexes. VII. Circular Dichroism in the Spin-forbidden Transitions of cis-[Cr(N)₆(O)₆]

Type Complexes with Ethylenediaminetetraacetic Analogues

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In our previous papers of this series,1-3 circular dichroism (CD) spectra in the spin-forbidden d-d transitions of trigonal and tetragonal Cr(III) complexes have been elucidated in comparison with those in the first spin-allowed d-d transitions by using the theoretical relations between the rotational strengths for the spin-forbidden and the spin-allowed transitions. No CD datum in the spin-forbidden transitions and few CD data in the spin-allowed transitions of chiral Cr(III) complexes with sexidentate ethylenediaminetetraacetic (edta) type ligands have been reported, whereas the CD spectra of several Cr(III) complexes with edta analogues have been studied and discussed in relation with their absolute configurations and theories of optical activity.5-7 To clarify these CD behavior, it is significant to reveal whether the CD in the spin-forbidden transitions of Cr(III) complexes with edta analogues will be elucidated in terms of the theoretical considerations for the rotational strengths in the d-d transitions on either the trigonal or tetragonal symmetry assumption. In this instance, it is desirable to examine the CD spectra in the spin-forbidden and the spin-allowed transitions of chiral Cr(III) complexes containing edta analogues with four glycinate rings as well as those of the known Cr(III) complexes,6 (−)α,β-trans-[Cr(O$_2$)]$^+$-ethylenediamine-N,N' diaceto-N,N'-dipropionatochromate(III), (−)α,β-[Cr(edda)]=[6], and (−)guanidino-trans-[Cr(S,S')-2,2'-(ethylenediamino)disuccinatochromate(III), (−)trans-[Cr(S,S'-edda)], both of which have two five-membered and two six-membered N-O chelate rings. Apart from some racemic complexes of the former type,8 no chiral Cr(III) complexes have yet been known.

This paper reports the preparation and stereospecific formation of a new chiral Cr(III) complex containing (25,45)-2,4-pentanediaminetetraacetic acid (S,S'-ptnta$^-$H$_3$,1,5H$_2$O) as one of the closely similar sexidentate ligands to the edta ligand. The CD data in the spin-forbidden transitions as well as in the spin-allowed transitions of this complex are examined together with those in the spin-forbidden transitions of chiral trans[Cr(O$_2$)] isoomers of (−)trans-[Cr(eddda)]=[ and (+)trans-[Cr(S,S'- edda)], of which the CD spectra in the spin-allowed transitions have been previously reported by Radanovic and Douglas.4 Their CD spectra in the whole region of the d-d transitions are compared with one another and discussed on the basis of both trigonal and tetragonal symmetry assumptions.

Experimental

Preparation of Ligands and Complexes. 1) (25,45)-2,4-pentanediaminetetraacetic Acid (S,S'-ptnta$^-$H$_3$,1,5H$_2$O): This ligand was prepared from (25,45)-2,4-pentanediamine by the method for the racemic one. Found: C, 43.77; H, 6.92; N, 7.63%. Caled for S,S'-ptnta$^-$H$_3$,1,5H$_2$O: C, 43.21; H, 6.97; N, 7.75%. 2) (+)trans-K[Cr(S,S'-ptnta)$_2$]·H$_2$O: To a solution of 1.0 g of S,S'-ptnta$^-$H$_3$,1,5H$_2$O in 15 cm$^3$ of water was added a solution containing 0.79 g of potassium hydroxide in 10 cm$^3$ of water. After dissolving 1.2 g of Cr(NO$_3$)$_3$·9H$_2$O in this solution at 70°C, the mixture was heated at 75-80°C with stirring for about 16 h. The color of the solution changed gradually from violet to red violet. By adding ethanol to this chilled solution, red powder was obtained. Recrystallization was performed from warm water and ethanol. Found: C, 35.29; H, 4.61; N, 6.36%. Caled for K[Cr(S,S'-ptnta)$_2$]·H$_2$O: C, 35.53; H, 4.59; N, 6.38%. 3) (−)trans-[Cr(S,S'-edda)]$^-$: The ligands, ethylenediamine-N,N' -diaceto-N,N'-dipropionionic acid (edda$^-$H$_3$)$_6$ and (S,S')-2,2'-(ethylenediamino)disuccinatochromate(III), (−)trans-[Cr(S,S'-edda)], were prepared by the reported methods. (−)trans-[Cr(eddda)]$^-$ and (−)trans-[Cr(S,S'-edda)]$^-$ were obtained by the method of Radanovic and Douglas.4 The absorption and CD spectra along with the infrared spectra confirm that these complexes are trans[Cr(O$_2$)] isoimers which have been previously established.4,10

Results and Discussion

Stereospecificity of [Cr(S,S'-ptnta)]$^-$. The visible absorption spectrum of [Cr(S,S'-ptnta)]$^-$ is quite similar in band position and intensities to that of the trimeth-
ON THE EMISSION AND THE EXCITATION SPECTRA OF SOME AROMATIC ESTERS

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The luminescence spectra of methyl-, ethyl-, propyl-, butyl-, and benzyl-benzoates, ethyl phenyl acetate, benzyl acetate and benzyl propionate have been studied in ethanol and in n-hexane rigid solutions at 77 K. In benzoic acid esters the fluorescence is very weak whereas the phosphorescence is intense. In the other esters, both the fluorescence and the phosphorescence appear with comparable intensity. The experimental results suggest that in these molecules the fluorescence and the phosphorescence are due to $S_1 \rightarrow S$ and $T_1 \rightarrow S$ transitions respectively. Phosphorescence excitation spectra show both $S \rightarrow S_{1g}$ and $S \rightarrow T_{1g}$ absorption bands for all the esters. In benzoic acid esters an additional absorption band has been observed. From the solvent effect on this band and from large $\Phi_P/\Phi_F$ values this has been assigned to the $S \rightarrow T_{1g}$ band.

1. Introduction

The luminescence properties of aromatic ketones, acids and aldehydes are of considerable interest because of the significant role played by the carbonyl group on radiative and non-radiative processes in these molecules [1–7]. In aromatic ketones and aldehydes [4, 6] mixing between the lowest triplet $T_{1g}$ state and the lowest excited singlet $S_{1g}$ state through spin–orbit interaction enhances the intensity of $T_{1g} \rightarrow S$ transitions. Because of the interesting behaviour of the carbonyl group we have investigated the luminescence spectra of a number of aromatic esters in which the position of the $=$C=O group relative to the phenyl ring differs. Phosphorescence excitation has been used to locate triplet states which lie above the lowest triplet state. The importance of these highly-lying triplet states in determining the rates of intersystem crossing makes such studies relevant to the theory of radiationless transitions. The work reported in this paper was undertaken to study the effect of the position of the $=$C=O group relative to the phenyl ring on the intensity of fluorescence and phosphorescence and to determine the location and assignment of the lowest, as well as any higher-lying, triplet states in these aromatic esters.

2. Experimental

The emission and excitation spectra were recorded on a Perkin–Elmer model MPF 44A fluorescence spectrophotometer (with photomultiplier tube R446 of Hamamatsu Corporation, Japan). Phosphorescence lifetimes were obtained from the decay of the photomultiplier signal as followed on a Perkin–Elmer 56 strip-chart recorder.

The aromatic esters studied were methyl-, ethyl-, propyl-, butyl-, and benzyl-benzoates, ethyl phenyl acetate, benzyl acetate and benzyl propionate. High quality chemicals were obtained from Fluka, Switzerland and Theodore Schuchardt, West Germany. The solvents used are spectrograde ethanol and n-hexane from E. Merck. The esters were fractionally distilled several times till no impurity could be detected with a flame ionisation detection column (Hewlett-Packard, model 5730A). The solutions were degassed by standard procedures [5] before running the spectra. The phosphorescence excitation method [7] has been used to get information about the states in these esters.

3. Results and discussion

The luminescence spectra of aromatic esters have
been studied in ethanol and n-hexane rigid solutions at 77 K using 2600 Å light from a high-pressure xenon arc as the exciting radiation. The ester concentration was typically 10^{-3} M. In all the aromatic esters both fluorescence and phosphorescence were observed. The emission spectra of some of these esters in ethanol rigid glass at 77 K are reproduced in figs. 1—3 without any photomultiplier sensitivity correction. The analyses of the spectra have been reported elsewhere [8], and it was concluded that the fluorescence in all these molecules arises from \( S_0 \rightarrow S \) transitions while the phosphorescence is due to \( T_{1} \rightarrow S \) transitions. The measured phosphorescence lifetimes (table 1) support this assignment. The relative intensities of the fluorescence and phosphorescence are quite different in benzoic acid esters from that in other esters. In the following paragraphs the significance of this observation is discussed.

In methyl-, ethyl-, propyl-, butyl-, and benzyl-benzoates, the fluorescence is very weak whereas phosphorescence is quite intense. In the other esters, namely in ethyl phenyl acetate, benzyl acetate and benzyl propionate, both fluorescence and phospho-
Table 1
Observed integrated intensity ratios of the phosphorescence and the fluorescence \((\Phi_p/\Phi_F)\), and mean phosphorescence lifetimes \((\tau_p)\) of aromatic esters \(^a\)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>In ethanol rigid solution at 77 K (concentration (10^{-3}) M)</th>
<th>In n-hexane rigid solution at 77 K (concentration (10^{-3}) M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Phi_p/\Phi_F)</td>
<td>(\tau_p) (s)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>methyl benzoate</td>
<td>54</td>
<td>2.5</td>
</tr>
<tr>
<td>ethyl benzoate</td>
<td>48</td>
<td>2.3</td>
</tr>
<tr>
<td>propyl benzoate</td>
<td>50</td>
<td>2.0</td>
</tr>
<tr>
<td>butyl benzoate</td>
<td>35</td>
<td>2.0</td>
</tr>
<tr>
<td>benzyl benzoate</td>
<td>32</td>
<td>2.5</td>
</tr>
<tr>
<td>ethyl phenyl acetate</td>
<td>0.7</td>
<td>5.3</td>
</tr>
<tr>
<td>benzyl acetate</td>
<td>3.0</td>
<td>3.8</td>
</tr>
<tr>
<td>benzyl propionate</td>
<td>3.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

\(^a\) \(\Phi_p/\Phi_F\) values are to be considered qualitative.

The observed integrated intensity ratios of phosphorescence and fluorescence for these aromatic esters are shown in table 1. In benzoic acid esters \(\Phi_p/\Phi_F\) is very large whereas in the other aromatic esters this ratio is small. The high values of \(\Phi_p/\Phi_F\) for benzoic acid esters and the low values in other esters indicate the importance played by the location of the carbonyl group on the luminescence properties of these molecules. In benzoic acid esters, the carbonyl group is attached to the phenyl ring and the excitation of the non-bonding electron localised on the oxygen atom of the \(\text{C}=\text{O}\) group gives a set of \(\pi\pi^*\) states. Existence of an \(\pi\pi^*\) triplet state above the lowest triplet state of \(\pi\pi^*\) type is known to affect the rates of intersystem crossing significantly \([4]\). So it may reasonably be suggested from the large \(\Phi_p/\Phi_F\) values in benzoic acid esters that, in these compounds, a \(T_{\pi\pi^*}\) state may lie above the lowest \(T_{\pi\pi^*}\) state but below the lowest \(S_{\pi\pi^*}\) state.

In ethyl phenyl acetate the \(\text{C}=\text{O}\) group is further away from the phenyl ring and is singly bonded to the carbon atom attached to the ring. In benzyl propionate and benzyl acetate the carbonyl group is further away from the ring and is singly bonded to an oxygen atom which in turn is singly bonded to a carbon atom attached to the ring. In these esters, conjugation across the single bonds is decreased significantly and no \(T_{\pi\pi^*}\) state between \(S_{\pi\pi^*}\) and \(T_{\pi\pi^*}\) states is available to enhance the intersystem crossing rate and both fluorescence and phosphorescence appear with comparable intensity. The importance of the interaction between the phenyl and the carbonyl part of benzoic acid has been emphasised by Maria and McGlynn \([5]\).

We have used the phosphorescence excitation method to study the \(S\leftarrow S\) and \(T\leftarrow S\) absorption spectra of the esters and some of these spectra are presented in figs. 1—3. The wavelength of the most intense band in the phosphorescence spectra (3900 Å in the case of benzyl benzoate) has been monitored to record the excitation spectrum. The authenticity of the \(S\leftarrow S\) and \(T\leftarrow S\) absorption bands was considered to be established when (i) the \(0\leftarrow 0\) band in the excitation spectrum overlapped the \(0\leftarrow 0\) band in emission and (ii) when the phosphorescence spectrum did not change with the wavelength of excitation lying in either the \(T\leftarrow S\) or the \(S\leftarrow S\) absorption regions.

It is observed (figs. 1 and 2) that in methyl and in benzyl benzoate, in addition to one \(T\leftarrow S\) absorption spectrum with its \(0\leftarrow 0\) band overlapping the \(0\leftarrow 0\) band of the phosphorescence spectrum, there lies an absorption band on the high energy side with origin at about 30998 cm\(^{-1}\) in methyl benzoate and at 30432 cm\(^{-1}\) in benzyl benzoate. Such a higher state has been observed in other benzoic acid esters. From the results presented in the previous section, i.e. large \(\Phi_p/\Phi_F\) values, it seems that this is a \(T_{\pi\pi^*}\) state. Such higher \(T_{\pi\pi^*}\leftarrow S\) transitions are generally 2—3 orders of magnitude stronger than \(T_{\pi\pi^*}\leftarrow S\) transitions \([7]\). We have observed this band to be considerably stronger than the lowest \(T_{\pi\pi^*}\leftarrow S\) band. The intense band of this system in benzyl benzoate is at 30294 cm\(^{-1}\) in...
$n$-hexane and at 30432 cm$^{-1}$ in ethanol glass. The blue-shift of the band in alcoholic solution adds credence to the assignment of the system to the $T_{n^*}$ state. In methyl benzoate and in some other benzoic acid esters this band appears broad but in benzyl benzoate the vibronic bands are resolved.

The upper state fundamentals observed in this band system can be satisfactorily correlated with the ground state fundamentals observed in emission. The vibronic bands in the upper $T_{n^*} + S$ transition are rather sharp in benzyl benzoate but the reason for the sharpness is not clear at this stage.

The excitation spectra of benzyl acetate are presented in fig. 3. This shows that even with the maximum sensitivity of the recording system no higher triplet states could be detected. Excellent overlap between the origin of the emission and excitation spectra has, however, been observed.

References

On the Luminescence Spectra of Some Aromatic Esters

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Received 13 February 1978; revised received 10 April 1978

The fluorescence and phosphorescence spectra of methyl-, ethyl-, propyl-, butyl-, and benzyl-benzoates and ethyl-phenyl acetate, benzyl acetate and benzyl propionate, have been investigated in ethanol and n-hexane rigid solutions at 77 K. From analyses of the vibrational structures of the fluorescence and phosphorescence spectra, and measured lifetimes of the phosphorescence emissions in these esters, it has been concluded that in all cases the fluorescence is due to an $S - T_{vib}$ transition while the phosphorescence emission occurs from a $T_{vib}$ state. Further, consideration of the relative intensities of the phosphorescence and the fluorescence emissions suggests that in the benzoic acid esters, in between the $S_{vib}$ and $T_{vib}$ states, there is an intervening $T_{vib}$ state which is not present in the other three esters.

It is now well established that the $>C=O$ group plays a dominant role on the luminescence properties of aromatic ketones and aldehydes. The $S - T_{vib}$ transitions in aromatic carbonyl compounds are considerably more intense than in the parent hydrocarbons. We have investigated certain aspects of luminescence spectra of a number of aromatic esters with carbonyl group attached to and separated from the phenyl ring because such studies are relevant to the theory of radiationless transitions in these molecules. In this note the results of an investigation of the effect of the position of the carbonyl group relative to the phenyl-ring on the structure and intensity of their fluorescence and phosphorescence emissions, are reported and discussed.

The emission spectra of the esters were recorded on a Perkin Elmer Model MPF 44A fluorescence spectrophotometer and their phosphorescence lifetimes were determined from the decay of the photomultiplier signals in the usual manner. The high quality aromatic esters; methyl-, ethyl-, propyl-, butyl- and benzyl-benzoates, ethyl phenyl acetate, benzyl acetate and benzyl propionate, were obtained from reputed firms and they were fractionally distilled several times till no impurity could be detected with a flame ionization detector column (Hewlett-Packard Model 5730A). The solvents used were spectrograde ethanol and n-hexane. In all cases the sample concentration was kept typically of the order of $10^{-8}$ M/l.

Fluorescence and phosphorescence spectra—The spectra of the aromatic esters were studied both in frozen solutions in ethanol and in n-hexane at 77 K. The typical spectra of a few molecules in ethanol glass are shown in Fig. 1 while tentative vibrational analyses of the emission spectra are presented in Tables 1 and 2.

Benzoic acid esters—Weak fluorescence with the (0, 0) band at 35188 cm$^{-1}$ in ethanol and at 35257 cm$^{-1}$ in n-hexane frozen solutions at 77 K has been observed in methyl-benzoate (Table 1). The spectrum shows two weak broad bands separated by a ground state fundamental frequency of 1064 cm$^{-1}$. On the other hand, the phosphorescence spectrum is intense and the band origin is at 27314 cm$^{-1}$ and 27329 cm$^{-1}$ in ethanol and n-hexane respectively. The spectra have been analyzed in terms of ground state vibrational frequencies 397, 961 and 1615 cm$^{-1}$, which are found to correlate well with the corresponding Raman and infrared data. The phosphorescence spectrum also contains bands which are combinations and overtones of the frequency 1615 cm$^{-1}$. The luminescence spectra of other benzoic acid esters are almost similar to that of methyl benzoate and hence are not discussed separately. From a comparison of the vibrational structures it is seen that in the fluorescence spectra of these esters, the only vibrational frequency observed is $\sim 1000$ cm$^{-1}$ and its value does not show significant change from molecule to molecule. This is correlated with the C—C breathing ring vibration. In the phosphorescence spectra, however, the fundamental frequency observed is 961 cm$^{-1}$ in methyl benzoate, 956 cm$^{-1}$ in ethyl-, 965 cm$^{-1}$ in propyl-, 960 cm$^{-1}$ in butyl- and 916 cm$^{-1}$ in benzyl-benzoate. This is definitely different from the C—C vibrations of the other benzoic acid esters.
Table 1—Luminescence Bands of the Benzoic Acid Esters at 77 K

<table>
<thead>
<tr>
<th>Molecule</th>
<th>In n-hexane Bands (cm⁻¹)</th>
<th>In ethyl alcohol Bands (cm⁻¹)</th>
<th>Tentative assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoate</td>
<td>3527 (vs) 2421 (vs) 0 2264 (s) 2259 (s) 0 2569 (s) 2569 (s) 0</td>
<td>35188 (vs) 35188 (vs) 0 26353 (s) 0 25693 (s) 25693 (s) 0</td>
<td>35188 (vs) 35188 (vs) 0 26353 (s) 0 25693 (s) 25693 (s) 0</td>
</tr>
<tr>
<td>Methyl</td>
<td>34271 (vs) 34201 (vs) 0 23302 (vs) 23222 (vs) 0</td>
<td>34201 (vs) 34201 (vs) 0 23222 (vs) 23222 (vs) 0</td>
<td>34201 (vs) 34201 (vs) 0 23222 (vs) 23222 (vs) 0</td>
</tr>
<tr>
<td>Benzyl</td>
<td>34791 (vs) 34762 (vs) 0</td>
<td>34762 (vs) 34762 (vs) 0</td>
<td>34762 (vs) 34762 (vs) 0</td>
</tr>
</tbody>
</table>

In ethanol glass at 77 K, the other benzoic acid esters show the fluorescence origin (Fo) and phosphorescence origin (Fo) and the fundamentals as follows:
- Ethyl: 35182 cm⁻¹ (Fo), 27299 cm⁻¹ (Fo); 389, 956, 999, 1600 cm⁻¹
- Propyl: 35171 cm⁻¹ (Fo), 27314 cm⁻¹ (Fo); 382, 965, 982, 1628 cm⁻¹
- Butyl: 35151 cm⁻¹ (Fo), 27337 cm⁻¹ (Fo); 398, 960, 997, 1605 cm⁻¹
- Benzyl: 35139 cm⁻¹ (Fo), 27307 cm⁻¹ (Fo); 242, 916, 973, 1621 cm⁻¹

breathing mode and possibly represents an out-of-plane C—H deformation vibration in these molecules. Besides, in the phosphorescence spectrum of each of these esters, a fundamental frequency at \( \sim 390 \text{ cm}^{-1} \) has been observed. This is close to the frequency 400 cm⁻¹ of the normal mode 16 A of benzene which represents an out-of-plane \( \text{C—C} \) deformation vibration.⁴ Thus our results show that some out-of-plane vibrations appear in the phosphorescence spectrum of these molecules.

Other Esters—Unlike in benzoic acid esters, in ethyl phenyl acetate, benzyl acetate and benzyl propionate esters, the fluorescence is very strong and comparable with the phosphorescence intensity (Fig. 1 and Table 2). Fairly good vibrational structure is revealed both in the fluorescence and phosphorescence spectra. The analysis of the fluorescence spectrum of ethyl phenyl acetate shows the presence of the fundamentals 616, 976 and 1599 cm⁻¹. These agree well with the observed strong Raman lines corresponding to 620, 999 and 1605 cm⁻¹. The phosphorescence spectrum of this molecule has been analyzed in terms of vibrational frequencies 1060 and 1599 cm⁻¹. The luminescence spectrum of benzyl acetate and benzyl propionate are similar as regards relative fluorescence and phosphorescence intensity and vibrational structure (Fig. 1 and Table 2). In benzyl propionate three fundamentals of frequencies 525, 956, 1583 cm⁻¹ are observed in fluorescence whereas only two fundamentals of 1052 and 1611 cm⁻¹ appear in the phosphorescence spectrum. The fundamentals 525 and 965 cm⁻¹ are correlated with the Raman lines 503 and 980 cm⁻¹ assigned to out-of-plane \( \text{C—C} \) and \( \text{C—H} \) deformation modes respectively.⁸ On the other hand, the fundamentals 1052 and 1583 cm⁻¹ which appear strongly in the Raman spectrum have been attributed to in-plane modes of vibration.

If all these ester molecules are considered to be planar having the symmetry \( \text{C}_s \), the electronic transitions in fluorescence and phosphorescence are \(^1A'\rightarrow^1A' \) and \(^3A'\rightarrow^1A' \) respectively and no out-of-plane mode is expected. The appearance of the out-of-plane vibrations in the emission spectra of these molecules suggests that these ester molecules probably belong to the point group \( \text{C}_1 \). It may also be noted that in the fluorescence and phosphorescence spectra of these esters no vibrational frequency due to the stretching of the carbonyl group has been found to appear. When a transition involves an \( n\pi^* \) state, the emission spectrum generally exhibits a prominent \( \text{C—O} \) vibrational progression.¹² Thus the vibrational structure of the emission spectra of these esters suggests that the \( n\pi^* \) states are involved in these transitions, i.e. the fluorescence is a \( S—S_n\pi^* \) and the phosphorescence is a \( S—S_n\pi^* \) transition.

Phosphorescence lifetimes \( \tau_p \)—Values of \( \tau_p \) of these esters were measured from the decay of the phosphorescence intensity with time. Except in initial time limited by the response time of the recording system, the decay was exponential and the mean lifetime was determined from this long time region of the phosphorescence decay. It is observed that the phosphorescence lifetime \( \tau_p \) of the benzoic acid esters in the frozen solutions at 77 K is typically about \( 2.3 \pm 0.2 \) sec. Under similar conditions, \( \tau_p \) for ethyl phenyl acetate is about \( 5.0 \pm 0.1 \) sec, whereas in each of the cases of benzyl acetate and benzyl propionate \( \tau_p \sim 3.8 \pm 0.2 \) sec. The long-lived phosphorescence of these esters indicates that the lowest triplet state in these cases is a \( n\pi^* \) state. This conforms to the conclusion.
Table 2—Luminescence Bands of Ethyl Phenyl Acetate and Benzyl Propionate at 77 K

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Fluorescence spectrum</th>
<th>Phosphorescence spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In n-hexane (cm⁻¹)</td>
<td>In ethyl alcohol (cm⁻¹)</td>
</tr>
<tr>
<td>Ethyl phenyl acetate</td>
<td>37302 (vwsh)</td>
<td>37372 (vwsh)</td>
</tr>
<tr>
<td>benzyl propionate</td>
<td>36686 (ms)</td>
<td>36780 (s)</td>
</tr>
<tr>
<td>acetate</td>
<td>36326 (vwsh)</td>
<td>36412 (vwsh)</td>
</tr>
<tr>
<td></td>
<td>35703 (vs)</td>
<td>35780 (vs)</td>
</tr>
<tr>
<td></td>
<td>34026 (wsh)</td>
<td>34090 (vwsh)</td>
</tr>
<tr>
<td></td>
<td>34796 (s)</td>
<td>34833 (vwsh)</td>
</tr>
<tr>
<td></td>
<td>337400 (w)</td>
<td>37414 (w)</td>
</tr>
<tr>
<td></td>
<td>36862 (s)</td>
<td>36898 (s)</td>
</tr>
<tr>
<td></td>
<td>36352 (msh)</td>
<td>36458 (msh)</td>
</tr>
<tr>
<td></td>
<td>34881 (ms)</td>
<td>34857 (ms)</td>
</tr>
<tr>
<td></td>
<td>35812 (s)</td>
<td>25912 (s)</td>
</tr>
<tr>
<td></td>
<td>25341 (msh)</td>
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<td></td>
<td>24806 (wsh)</td>
<td>24868 (wsh)</td>
</tr>
<tr>
<td></td>
<td>24335 (wsh)</td>
<td>24393 (vwsh)</td>
</tr>
<tr>
<td></td>
<td>28935 (w)</td>
<td>28977 (w)</td>
</tr>
<tr>
<td></td>
<td>27870 (ms)</td>
<td>27925 (ms)</td>
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<td></td>
<td>27333 (wsh)</td>
<td>27366 (s)</td>
</tr>
<tr>
<td></td>
<td>26383 (vw)</td>
<td>26744 (vwsh)</td>
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<tr>
<td></td>
<td>26333 (s)</td>
<td>26377 (vs)</td>
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<tr>
<td></td>
<td>25773 (ms)</td>
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<td>25357 (w)</td>
<td>25341 (s)</td>
</tr>
<tr>
<td></td>
<td>24738 (vwsh)</td>
<td>24776 (vwsh)</td>
</tr>
<tr>
<td></td>
<td>24199 (vwsh)</td>
<td>24217 (vwsh)</td>
</tr>
</tbody>
</table>

In ethanol glass at 77 K, benzyl acetate shows origins (F₀ & P₀) and the fundamentals as:
37442 cm⁻¹ (F₀), 28998 cm⁻¹ (P₀) : 553, 1050, 1585 cm⁻¹.

Drawn above under the section entitled 'Fluorescence and phosphorescence spectra'. An interesting feature of these spectra is that, in the benzoic acid esters, the phosphorescence is much more intense than the fluorescence while in ethyl phenyl acetate, benzyl acetate and benzyl propionate the intensities of the two emissions are comparable. In the benzoic acid esters, the carbonyl group is attached to the phenyl ring and the excitation of the non-bonding electron localized in the oxygen atom of the \( \overset{\sim}{-}C=O \) group gives a set of \( n^* \) states. Location of such a \( n^* \) triplet state above the lowest triplet state of \( \pi^* \) type is known to affect the rate of intersystem crossing significantly. Very weak fluorescence and intense phosphorescence in benzoic acid esters show that a \( T_{\pi^*} \) state lies in between the lowest singlet \( S_{\pi^*} \) and the lowest triplet \( T_{\pi^*} \) states wherefrom phosphorescence arises. In ethyl phenyl acetate the \( >C=O \) group is away from the phenyl ring and is singly bonded to a carbon atom attached to the ring. In benzyl propionate and benzyl acetate the carbonyl group is still further away from the ring and is singly bonded to an oxygen atom which, in turn, is singly bonded to a carbon atom attached to the ring. In these esters, conjugation across the single bonds may decrease significantly so that \( S_{\pi^*} \) or \( T_{\pi^*} \) type of states do not occur and efficient intersystem crossing through an intervening \( T_{\pi^*} \) state cannot take place in these molecules.

References
On the origin of some anomalous luminescence behavior of isomeric cyanopyridines

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The results of a comparative study of the absorption and emission properties and the triplet yields of the isomeric cyanopyridines (CNP) and benzonitrile under various environmental conditions are reported. All the three CNP isomers are found to be nonfluorescent but exhibit a fairly strong phosphorescence emission of \( \pi^* \) character in rigid polar media at 77 K. \( \Phi_p \) values of the CNP are found to be sensitively dependent on the rigidity (or viscosity) and crystalline structure of the solvent medium. Whereas the 3-CNP molecule phosphoresces with moderately strong intensity in hydrocarbon solvents, the 2 and 4 isomers are completely nonluminescent in glassy or highly disordered crystalline phases of hydrocarbons, e.g., n-alkanes, cyclohexane (CH), and methylcyclohexane (MCH). A dramatic reappearance of the phosphorescence emission from these two isomers (with anomalously large red-shifted spectral positions) has, however, been observed in crystalline CH and MCH matrices. Unlike the 3 isomer, both the 2- and 4-CNP have been found to exhibit phosphorescence in pure crystalline form at 77 K. The \( n^*, \pi^* \) electronic states associated with the pyridinic nitrogen atom have been identified in the absorption (or excitation) spectra and shown to be responsible for the nonluminescent nature and the high triplet yields (\( \Phi_p \sim 0.8 \)) of CNP molecules. A tentative interpretation of the diverse emissive characteristics of cyanopyridines has been offered in terms of the predominance of the effect of pseudo-Jahn–Teller distortion and the matrix potential in governing the radiative and radiationless deactivation of the lowest triplet state of these molecules. The distinctive differences observed in the emissive characteristics of the 3-CNP and other two isomers have been attributed to the differences in the distortability of the conformational mobility of the CNP isomers arising primarily as a result of inductive effects of the pyridinic nitrogen atom and the nitrile group.

INTRODUCTION

Unlike those of their phenyl counterpart, many substituted pyridine compounds exhibit peculiar luminescence properties. For example, although pyridine is generally considered to be nonluminescent, some of its derivatives with electron-donating substituents such as \(-\text{OCH}_3\), \(-\text{NH}_2\), \(-\text{OC}_6\text{H}_5\), etc. are known to exhibit observable fluorescence and phosphorescence emissions in rigid polar media.\(^1\)\(^-\)\(^4\) These compounds, however, seem to be completely nonluminescent in hydrocarbon matrices, e.g., methylcyclohexane.\(^1\)\(^-\)\(^4\) Hoover and Kasha\(^5\) have also reported similar nonluminescent behavior of some methyl derivatives of pyridine in hydrocarbon matrices at 77 K. Besides this intriguing feature, there exist marked dissimilarities in the emission characteristics and the nature of the lowest excited states amongst isomers of the same compound. In the case of isomeric hydroxypyridines, Weisstuch et al.\(^6\) have noted that while 2-hydroxypyridine fluoresces in all the solvents used by them and the 3 isomer emits only in aqueous solution, 4-hydroxypyridine remains nonfluorescent in any of the solvents. With aminopyridines, Testa et al.\(^7\) have shown that the 2 and 3 isomers exhibit predominantly \( \pi^*, \pi^* \) character in their lowest excited singlet state, while the 4 isomer possesses a lower lying \( \pi^*, \pi^* \) state.

Although the nature of the lowest triplet states of hydroxy, methoxy, and aminopyridines has been well characterized, there seems to be some concern as to the correct assignment of the lowest triplet states of some substituted pyridines with electron-withdrawing groups, such as the cyanopyridines (CNP). The results of two rather preliminary studies\(^8\)\(^-\)\(^6\) of these compounds have led to the contradictory assignment of the lowest triplet state for one of the isomers (4-CNP): the \( n^*, \pi^* \) and \( \pi^*, \pi^* \) assignments on the basis of its phosphorescence lifetime\(^5\) and the phosphorescence decay rate and zfs data,\(^6\) respectively. This CNP isomer also shows values of the phosphorescence decay rate and zfs distinctly different from other two isomers and anomalously high.\(^6\) However, except for these few fragmentary data, detailed information concerning the luminescence properties of the CNP molecules are scantily available in the published literature, emphasizing the need for further investigation of these compounds.

Cyanopyridines are of considerable photochemical interest.\(^7\) From a spectroscopic point of view these molecules also seem important, because, in these molecules, in addition to the strongly electron-withdrawing and mesomeric nitrile group there is attached to the aromatic ring a strongly inductively electron-withdrawing nitrogen atom, and it is expected that the effects of intramolecular interactions arising as a result of strong vibronic and spin–orbit coupling between the \( \pi^*, \pi^* \) and \( \pi^*, \pi^* \) electronic states and the inductive perturbation of these electron-withdrawing groups would be reflected in the spectral characteristics of these molecules.

In view of the conflicting assignment of the lowest triplet state of CNP and the highly solvent dependent luminescence behavior of the pyridine compounds, a detailed examination of the absorption and emission characteristics of the cyanopyridines in a variety of environmental conditions has been carried out. Similar studies on their phenyl analog benzonitrile were also made under identical experimental conditions for comparison. One of the principal objectives of this study is to investigate the role played by the pyridinic nitrogen atom and its associated \( n^*, \pi^* \) electronic states in deter-
Sarkar, Ghoshal, and Kastha: Luminescence of isomeric cyanopyridines

The intersystem crossing yields of these cyanopyridines in glassy hydrocarbon matrices (e.g., MCH) were determined following the method described by Favaro. With the CNP (~10^{-4} M) as energy donors and biacetyl (~10^{-3}-10^{-4} M) as the acceptor, the triplet yields (ΦT) of the CNP molecules were estimated (assuming unitary triplet yields for benzophenone) from the efficiency of these molecules in sensitizing the biacetyl phosphorescence. The authenticity of energy transfer from the lowest triplet states of the cyanopyridines to the singlet state of biacetyl molecule was established from the observation that (i) the excitation spectra, obtained by monitoring the sensitized phosphorescence band (525 nm) of biacetyl, corresponded to the phosphorescence excitation spectra of the cyanopyridines, and (ii) there is considerable overlap between the T-S0 systems of the CNP and the S(n, n*)-S0 band system of biacetyl.

FIG. 1. Vapor-phase absorption spectra of 4-CN? (-----) and benzonitrile (-----) at 330 K and 0.1 Torr.

RESULTS

Absorption characteristics

In the vapor phase absorption spectra of all the cyanopyridines and benzonitrile (Fig. 1), two distinct band systems corresponding to S3(ir, n*)-S0(1La) and S3(ir, ir*)-S0(1I,6) transitions are observed. In contrast to the sharp and structured absorption bands exhibited by benzonitrile, the 1La band systems of all the CNP molecules are found to be rather broad and diffuse. In the solution spectra, the absorbance and the oscillator strength of the 1La bands of all the isomers are significantly greater than that of benzonitrile. The 1La bands of each of the cyanopyridines are very sharp and structured, but the 0,0 band is found to appear at substantially higher frequency relative to that of benzonitrile. Details of the spectral data are given in Table I.

Besides these distinctive spectral features, very weak absorption bands corresponding to S1(w, n*)-S0 transition with origin at 29,790 cm^{-1} and partially obscured by the overlapping n, n* bands have been observed in the vapor phase spectrum of 4-CN? molecule only. Such overlapping n, n* bands have also been detected in the room temperature (300 K) absorption spectra of hydrocarbon solutions of the 3- and 4-CNP at higher concentrations (~10^{-4} M), except for the 2 isomer. In protic solvents, the 1La bands of the CNP molecules appear with a little more resolved structure (Fig. 2) presumably as a result of marked inhibition of the overlapping n, n* bands due to intermolecular hydrogen-bond formation in these media.

The phosphorescence excitation spectra of the CNP molecules in rigid polar media (Figs. 3-5) reveal to a greater extent the effect of intermolecular hydrogen-
TABLE I. Absorption data\textsuperscript{a} of cyanopyridines and benzonitrile.

<table>
<thead>
<tr>
<th>Mole,</th>
<th>(0\rightarrow 0) energy (cm(^{-1}))</th>
<th>(v(N=C)) (cm(^{-1}))</th>
<th>(\epsilon (f))</th>
<th>(0\rightarrow 0) energy (cm(^{-1}))</th>
<th>(\epsilon (f))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{F-CN})</td>
<td>44 629</td>
<td>45 494</td>
<td>1932</td>
<td>9.794(0.12)</td>
<td>36 518</td>
</tr>
<tr>
<td>(2\text{-CNP})</td>
<td>45 983</td>
<td>44 529</td>
<td>1915</td>
<td>9.536(0.10)</td>
<td>37 232</td>
</tr>
<tr>
<td>(3\text{-CNP})</td>
<td>45 234</td>
<td>44 332</td>
<td>1743</td>
<td>9.793(0.16)</td>
<td>37 094</td>
</tr>
<tr>
<td>(4\text{-CNP})</td>
<td>46 549</td>
<td>45 337</td>
<td>1762</td>
<td>11 984(0.16)</td>
<td>36 090</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Absorption measurements were made at 300 K. The symbol \(\epsilon\) refers to the extinction coefficient (in 1 mol\(^{-1}\) cm\(^{-1}\)) and the symbol \(f\) to oscillator strength.

In addition to the readily observable \(S_1\rightarrow S_0\) and \(S_2\rightarrow S_0\) band systems, relatively weak but distinct bands attributable to \(T\rightarrow S_0\) absorption have been observed in the phosphorescence excitation spectrum of each of the cyanopyridines. Of these two bands, the lower energy one is very close to and overlaps the phosphorescence band origin and the other lies within a few hundred wave numbers to the higher energy side of the former. A part of the phosphorescence excitation spectra of the \(4\text{-CNP}\) in a series of solvents with increasing polarity (viz., ethanol< water< 1\% HCl in ethanol) at 77 K are shown in Fig. 3. The observation that the intensity of the lower energy band remains almost unaltered while the higher energy band undergoes noticeable obliteration upon increasing the polarity of the solvent leads to the attribution of these bands to \(n, \pi^*\rightarrow S_0\) and \(n, \pi^*\rightarrow S_0\) transitions, respectively. The excitation spectra of the other two isomers also exhibit similar features and their \(n, \pi^*\) and \(\pi, \pi^*\) bands have been identified analogously. In the case of \(3\text{-CNP}\), where the phosphorescence excitation spectrum could be recorded in both hydrocarbon and hydroxyl solvents, the significant blue shift of the higher energy band observed, upon changing the solvent from hydrocarbon to ethanol, also lends credence to the \(n, \pi^*\) assignment of the latter band. A weak band corresponding to \(T\rightarrow S_0\) absorption has also been observed in the phosphorescence excitation spectrum of benzonitrile, but the intensity of such bands in the case of CNP molecules has been found to be at least one order of magnitude greater than that of benzonitrile under identical conditions. The relative positions of the energy levels of the singlet and triplet states of these molecules in polar and nonpolar solvents are shown in Table II.

Emission characteristics

With \(1L_a\) excitation all the isomeric cyanopyridines exhibit fairly intense phosphorescence emission in rigid
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FIG. 4. Phosphorescence and phosphorescence excitation spectra, polarized phosphorescence (PP) and excitation (PE) spectra of 2-CNP at 77 K. P: Phosphorescence (-----) in ethanol; (------) in crystalline MCH. Excitation spectrum: (-----) in ethanol; (-----) in crystalline MCH. PP and PE: (-----) in EPA glass.

polar media at 77 K. The phosphorescence lifetime ($\tau_P$) of each of the isomers has been found to be of the order of a second. The phosphorescence spectra of 2-, 3-, and 4-cyanopyridines in ethanol glass at 77 K are shown in Figs. 4-6; data pertaining to these spectra are collected in Table II. In contrast to benzonitrile, which exhibits highly structured fluorescence and phosphorescence emissions of comparable intensity in every standard polar and nonpolar solvents, all the isomeric cyanopyridines are almost nonfluorescent (within detectable limit) in polar as well as in nonpolar media. Further, while the phosphorescence intensity of benzonitrile remains almost comparable in most of the solvents used, a marked enhancement in the phosphorescence intensity of the CNP molecules has been observed in going from ethanol to more rigid polar medium, such as water at 77 K (cf. Table III).

The 3-CNP molecule exhibits phosphorescence emission of moderate intensity in every polar as well as nonpolar, hydrocarbons, whereas the 2 and 4 isomers are completely nonluminescent in glassy phases of CH and MCH or in Shpol'skii matrices at 77 K. Perhaps the most interesting aspect of the luminescence behavior of the 2 and 4 isomers is the dramatic reappearance of their phosphorescence emission in crystalline CH or MCH matrices at 77 K. In these cases, however,

![Graphical representation of phosphorescence and phosphorescence excitation spectra for 2-CNP, 3-CNP, and 4-CNP at 77 K.](image)

TABLE II. Observed energy values of singlet and triplet levels of cyanopyridines and benzonitrile from phosphorescence excitation spectra at 77 K.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$E_{1L_2}$ in cm$^{-1}$</th>
<th>$E_{1H, \pi^*}$ in cm$^{-1}$</th>
<th>$E_{3H, \pi^*}$ in cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecules</td>
<td>EOH</td>
<td>CH</td>
<td>MCH</td>
</tr>
<tr>
<td>2-CNP</td>
<td>36 955 (32 196)</td>
<td>34 472</td>
<td>34 893</td>
</tr>
<tr>
<td>3-CNP</td>
<td>36 455</td>
<td>36 619</td>
<td>36 592</td>
</tr>
<tr>
<td>4-CNP</td>
<td>35 052 (31 338)</td>
<td>34 472</td>
<td>31 437</td>
</tr>
<tr>
<td>$\phi$-CN</td>
<td>35 831</td>
<td>36 990</td>
<td>36 025</td>
</tr>
</tbody>
</table>

aData in crystalline phases of cyclohexane (CH) and methylcyclohexane (MCH) except for 3-CNP.

bData in pure crystalline forms.

large red shifts of the \( n, \pi^* \) and \( \pi, \pi^* \) singlet and triplet energy levels. The striking resemblance in the appearance of the phosphorescence spectra in ethanol glass and crystalline MCH matrices and the lack of any concentration effect in the \( 10^{-6}-10^{-4} \) M range suggest that such a large spectral shift cannot be attributed to the effect of dimer formation. In this context, it is interesting to note that, in contrast to 2 and 4-cyanopyridines the MCH solution of the 3 isomer could not be crystallized by the procedure adopted for other two isomers, and the solution remained predominantly in the glassy phase of clear transparency. Also, except for a small solvatochromic shift no appreciable change in the spectral position of the phosphorescence spectrum of 3-CNP has been observed in MCH matrix at 77 K. However, the phosphorescence yield of the 3 isomer in hydrocarbon matrices has been found to be significantly less than that in ethanol glass.

Another distinct feature posed by the 3-CNP molecules is that while both the 2 and 4 isomers exhibit a moderately strong phosphorescence emission in pure crystalline form at 77 K, no perceptible emission from rigorously purified 3-CNP crystals is observed. It is noteworthy that the phosphorescence emissions from crystalline samples again appear at considerably red-shifted spectral positions (Table III).

The phosphorescence polarization curves (Figs. 4-6) show that the phosphorescence of all the isomeric CNP is negatively polarized with respect to \( ^1L_u \) excitation. This strongly indicates the predominantly out-of-plane polarization of the phosphorescence emission of these molecules. The significant alteration in the degree of polarization (\( P_\lambda \)) outside the 0-0 band also implies the occurrence of vibronic activity of nontotally symmetric modes in the phosphorescence emissions of cyanopyridines. The effect is however, more pronounced in the case of the 4 isomer and the shoulder at 815 cm\(^{-1}\) in the

---

**TABLE III.** Measured values of phosphorescence band origins, mean phosphorescence lifetime (\( \tau_p \)), and quantum yield (\( \Phi_p \)) of cyanopyridines and benzonitrile.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Phosphorescence band origins cm(^{-1})</th>
<th>77 K</th>
<th>Fundamental frequencies cm(^{-1})</th>
<th>77 K</th>
<th>93 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Phi-CN )</td>
<td>27069</td>
<td>24899</td>
<td>24930</td>
<td>698</td>
<td>956</td>
</tr>
<tr>
<td>2-CNP</td>
<td>27069</td>
<td>24899</td>
<td>24930</td>
<td>698</td>
<td>956</td>
</tr>
<tr>
<td>3-CNP</td>
<td>27070</td>
<td>27055</td>
<td>26910</td>
<td>1623</td>
<td>1945</td>
</tr>
<tr>
<td>4-CNP</td>
<td>27025</td>
<td>26309</td>
<td>26102</td>
<td>815</td>
<td>585</td>
</tr>
<tr>
<td>( \Phi-CN )</td>
<td>27070</td>
<td>27019</td>
<td>26953</td>
<td>1019</td>
<td>1231</td>
</tr>
</tbody>
</table>

*Data in crystalline phases of cyclohexane (CH) and methylcyclohexane (MCH) except for 3-CNP.*

*Data in pure crystalline forms.*

*C=N stretching frequency.*
phosphorescence spectrum of this molecule in EtOH represents such a vibrational mode. This most likely corresponds to an out-of-plane C-H bending vibration of the molecule.

The predominantly out-of-plane polarization of the phosphorescence emission and the solvent shifts of the phosphorescence and \( T^* - S_0 \) excitation spectra of the CNP molecules coupled with their respective long phosphorescence lifetimes clearly indicate that the lowest triplet state of each of the isomeric cyanopyridines to be \( ^3\pi, ^3\pi^* \) in nature. The findings of a recent ODMR study \(^6\) of these compounds are in conformity with these views.

From the energy-transfer experiment, the measured values of the triplet yields of the cyanopyridines are observed to be as high as 0.8 ± 0.05 for 2- and 3-CNP and 0.85 ± 0.05 for 4-CNP.

**DISCUSSION**

The distinctive differences in the spectral characteristics of the CNP molecules and their phenyl analog benzonitrile observed in the present study are clearly attributable to the effects of some intramolecular interactions arising as a result of the pyridyl nitrogen atom and its associated \( n, \pi^* \) electronic states. Because of the presence of nearby but lower lying \( n, \pi^* \) electronic states in cyanopyridines, it is expected that there should occur a strong vibronic interaction between the \( ^3\pi, ^3\pi^* \) and \( n, \pi^* \) states of these molecules. The noticeable broadening of the \(^1L_0\) bands observed in the absorption and excitation spectra of cyanopyridines is indicative of the occurrence of such vibronic interaction\(^7\) in the singlet manifold of these molecules. The presence of out-of-plane vibrations in the phosphorescence spectra, the remarkable enhancement of intensity of the \( T^* - S_0 \) band in the excitation spectra, and the relatively short phosphorescence lifetimes of the CNP molecules compared with that of benzonitrile observed also clearly signify the occurrence of strong vibronic interactions in the triplet manifold of these molecules. This is also implicit from their \( T_2(n, \pi^*) - T_1(\pi, \pi^*) \) energy separation data (Table II). The effects of such vibronic interaction have, however, been found to be much more pronounced in the case of 4-CNP. It may also be noted that to account for the anomalously high \( x\pi \) values and the phosphorescence decay rate constant of this isomer, the assumption of strong vibronic interaction between the close lying \( n, \pi^* \) and \( \pi, \pi^* \) triplets was compelling.\(^8\)

The relative dispositions of the \( n, \pi^* \) and \( \pi, \pi^* \) singlet and triplet energy levels, so found in the case of all the CNP isomers and the strong vibronic interactions between the \( n, \pi^* \) and \( \pi, \pi^* \) states are expected to constitute, in accordance with the theoretical concepts,\(^9\) a very fast and efficient excitation pathway for the radiationless deactivation of the excited singlet states through the intersystem crossing and internal conversion processes. As a consequence, excitation into the respective \( S_0(\pi, \pi^*) \) states of CNP molecules leads to a very fast and efficient population of the lowest triplet states and the molecules are thereby rendered nonfluorescent. The high phosphorescence and triplet yields (Table III) observed for cyanopyridines are substantive of the occurrence of very rapid and efficient intersystem crossing process in these molecules.

However, the large environmental dependence of the phosphorescence yields, particularly the complete non-luminescent behavior of the 2 and 4 isomers in glassy hydrocarbon or Shpolskii matrices suggests that, depending upon the nature of the solvent medium the \( T_1 - S_0 \) radiationless deactivation process could also be very efficient in these molecules. From the phosphorescence excitation spectrum it is seen that in ethanol glass the \( n, \pi^* \) and \( \pi, \pi^* \) triplet levels of 2-, 3-, and 4-CNP are separated by ~900, 1100, and 570 cm\(^{-1}\), respectively; while this energy gap is only ~400 cm\(^{-1}\) in the case of 3-CNP in MCH glass. Thus a \( \Delta n \approx 700 \text{ cm}^{-1} \) accounts for the relative solvatochromic shifts of the \( n, \pi^* \) and \( \pi, \pi^* \) states of 3-CNP in going from ethanol to MCH glass at 77 K. Now, if it is assumed that the triplet states of other two isomers would also undergo solvatochromic shifts of comparable magnitude, the two triplet states of 2- and 4-CNP would then be expected to lie within ~200 cm\(^{-1}\) (in the case of 4-CNP these may be considered to be almost degenerate) in MCH glass.

At this \( T_2 - T_1 \) energy separation strong vibronic interactions of the pseudo-Jahn-Teller type are expected to occur, as has been postulated for several aromatic azines\(^16\) and carbonyl compounds.\(^17\) If such vibronic interaction is sufficiently strong it can cause considerable distortions in the potential surface of the lowest triplet state, and consequently may lead to a pronounced enhancement of the \( T_2 - S_0 \) radiationless deactivation.

Such spectral manifestations of the pseudo-Jahn-Teller effect are well known, particularly in the case of azoaromatics and, in fact, have been used by many earlier investigators\(^16\) to explain the highly solvent dependent luminescence behavior of these compounds. In consequence, the completely nonluminescent behavior of the 2- and 4-CNP in glassy hydrocarbon matrices seems most likely related with this spectral manifestation of the pseudo-Jahn-Teller effect.

The occurrence of a relatively much weaker phosphorescence emission from 3-CNP in hydrocarbon matrices compared to those observed in rigid polar media implies a substantial \( T_1 - S_0 \) radiationless deactivation of this isomer presumably as a manifestation of the pseudo-Jahn-Teller effect but to a lesser extent than those observed for other two isomers in hydrocarbon matrices. This is also implicit from the relatively larger \( T_2 - T_1 \) energy separation for this isomer compared to those of other two CNP isomers.

The marked variation of the phosphorescence yields of the CNP molecules with changes in the viscosity (or rigidity) and crystalline structure of the host medium (cf. Table III) strongly suggests that the solvent cage constraint or the matrix potential assumes a prominent role in determining the radiative and radiationless deactivation of the lowest triplet states of these molecules. It appears that the rigidity of the solvent cage or crystal field constraints might be controlling the efficiency of the \( T_1 - S_0 \) radiationless deactivation of the solute CNP.
molecules presumably by inhibiting the relaxation process.

The relaxed hydrocarbon matrices such as the glassy phases of CH or MCH or the Shpolskii matrices approximate to an inert, weakly interacting environment where the solute CNP molecules may have considerable freedom for configurational relaxation. These matrices thus provide an environment suitable for the effective functioning of the pseudo-Jahn–Teller effect. And as the CNP molecules can undergo molecular distortions (an important step for at least one path for radiationless decay) under the action of the pseudo-Jahn–Teller effect, a pronounced enhancement of the $T_{1r} \rightarrow S_0$ radiationless deactivation of the CNP molecules occurs in these media.

Because of the larger energy gap between the $3\pi, \pi^*$ and $1\pi, \pi^*$ states of cyanopyridines in rigid polar media (e.g., ethanol and water), the vibronic interaction between these states is expected to be reduced in such media. Secondly, since the rigidity of the solvent cage also tends to prevent the conformational changes of the solute (CNP) molecules, the effect of pseudo-Jahn–Teller distortion becomes much less effective in these media.

In crystalline media, the host–guest picture is somewhat different from that envisaged in the case of glassy media. It is known that substitutional incorporation of guest molecule into the host crystal lattice can cause appreciable distortions in the molecular structure or in the crystal lattice unless both the guest molecules are isomorphous and dimensionally identical. An analysis of the spectral data of cyanopyridines in crystalline CH and MCH matrices suggests that on entering into the lattice of CH and MCH crystals the molecules of 2- and 4-CNP isomers must have undergone substantial distortions and that unlike those of the glassy phases of CH and MCH, the matrix potential is quite large in these cases. It seems therefore reasonable to expect that such a large crystal packing induced molecular distortions in the ground state of these molecules in crystalline CH and MCH would be strong enough to outweigh the effect of pseudo-Jahn–Teller type of distortions. Moreover, from the excitation spectra, it is seen that the near degeneracy between the $\pi, \pi^*$, $\pi^*-\pi$, $\pi^*$ triplets of 2- and 4-CNP no longer prevails in this situation. Thus, because of the less effective functioning (or the absence) of the pseudo-Jahn–Teller effect, phosphorescence emissions possibly occur from the distorted molecules--these CNP isomers in crystalline CH and MCH matrices.

The markedly red-shifted spectral position of the phosphorescence emissions from pure 2- and 4-CNP crystals at 77 K seems to suggest that the origin of such emissions is mostly likely the molecular traps of the distorted CNP molecules trapped into their respective crystal lattices. The absence of any phosphorescence emission from pure 3-CNP crystal therefore signifies that these "K-traps" are probably not found in this crystal.

To better understand the influences of the matrix potential on the radiative and nonradiative processes of cyanopyridines, a complementary study of the response of phosphorescence emission to the changes in viscosity and crystalline structure of the host medium was carried out. For this purpose, we are guided by the fact that both CH\textsuperscript{19} and MCH\textsuperscript{20} are known to undergo polymorphic phase transitions and the expectation that the viscosity of ethanol glass should decrease rapidly with the rise of temperature in the low temperature ranges.\textsuperscript{21}

In fact, a close inspection of the plots of variation of the phosphorescence intensity of cyanopyridines and benzonitrile (Fig. 7) with the progressive rise of ambient temperature (ethanol, CH, and MCH as host media) have revealed particularly striking features: For both the cases of crystalline CH and MCH matrices, the phosphorescence intensity, instead of decreasing monotonically, undergoes a dramatic variation with well-defined peaks and minima. The peaks around the temperatures 115 and 196 K for CH and 85 and 152 K for MCH most likely correspond to the optimum temperatures for the existence of two crystalline forms of CH and MCH, respectively; while the minimum at 186 K observed in the curve for CH and at 130 K for MCH signifies their phase transition temperatures. The significant enhancement of the phosphorescence of 2 and 4 isomers at the peak temperatures may be associated with the maximum percent incorporation of these molecules in the lattices of the corresponding stable crystalline form of CH and MCH.
In ethanol glass, in contrast to that observed for the 3-CNP, the phosphorescence intensity of the 2 and 4 isomers suffer a steep fall in the 77–100 K range. This implies that the relaxation and quenching processes in 2- and 4-CNP are more efficient than in the 3 isomer. Presumably, the distortability or conformational mobility of the former two isomers are greater than that of the 3-CNP. As a consequence, concomitant with the decrease of solvent viscosity, there occurs the cage relaxation which leads to the efficient quenching of the phosphorescence emission for these two isomers. The nature of variation of the phosphorescence intensity with the decrease of solvent viscosity in the case of benzonitrile is similar to that of the 3-CNP. The results of this experiment and also the fact that the 3-CNP molecules are incapable of entering into the crystal lattices of CH and MCH and that no emission attributable to the distorted molecular geometry occurs from this kind of molecules appear to dictate a relatively more rigid molecular structure for this isomer.

From the analysis of the results so far described, a close correlation between the structural and the emissive characteristics of 2- and 4-CNP and the distinct differences in these properties between these two isomers and the 3-CNP are quite apparent. Thus the relative positions of the pyridinic nitrogen atom and the nitrile group in cyanopyridines seem important in determining the luminescence properties of these molecules. It appears that the origin of all the diverse emissive characteristics of the CNP isomers might be intimately related with the position dependent perturbing influences of the ring nitrogen atom.

Benzonitrile is considered to be representative of the substituted benzene with strongly mesomeric and electron-attracting substituent. There exists, in benzonitrile, as well as in cyanopyridine, a strong s conjugation between the nitrile group and the aromatic ring. The higher energy singlet \( \pi^* - \pi \) transition (\( 1L_\text{u} \)) of benzonitrile is also known to possess both intramolecular charge transfer character and local excitation character. In cyanopyridines, because of the presence of strongly electron-withdrawing nitrogen atom in the aromatic ring, it is expected that the migration of electrons towards the \(-\text{CN}\) group would be rendered difficult. A clear reflection of this effect is seen in the absorption spectra corresponding to \( 1L_\text{u} \) bands of CNP where substantial shifting of these bands to higher frequencies compared to that of benzonitrile has been observed (Table I).

Because of the strongly electron-withdrawing nature of the nitrile group and the pyridinic nitrogen atom in cyanopyridines, a strong inductive conjugation between these two groups is expected to occur in these molecules. In 3-cyanopyridine, these two groups being mutually at meta position are in most favorable position to meet their electron demand. Since the inductive effects of these two groups are cooperative, they reinforce each other leading to the stabilization of the electronic states and molecular geometry of this isomer. In the case of 2- and 4-CNP, on the other hand, these two groups tend to counteract each others’ effect on account of their relative positions not being so favorable for the \(-\text{CN}\) charge redistribution around the ring. It is possible that some steric effect owing to a stronger conjugation of the CN group with \( \pi \) orbitals of the phenyl ring might also be responsible for the greater geometrical stability of the 3 isomer. The significant decrease in the CN bond length of 3-CNP compared to that of 4-CNP obtained from the x-ray structural analyses and the presence of bands corresponding to the \(-\text{CN}\) stretching frequency (Table III) may be adduced as evidence in support of this view.

In conclusion, the results of this study show that similar to those of many aza-aromatics the radiationless deactivation processes in cyanopyridines are very efficient. These molecules have also proved to be very efficient energy donors, so much so that even a trace amount of impurity present either in these compounds or in solvents gives rise to impurity emission. Although the interpretation of the anomalous luminescence properties of these molecules put forward here is necessarily tentative, it can be said that most of the emissive characteristics exhibited by the isomeric CNP molecules could satisfactorily be explained, at least qualitatively, in terms of the combined effect of the pseudo-Jahn-Teller interaction and the environmental potential. Both these factors seem to be important in determining the luminescence properties of these molecules.


