

$$B = \frac{1}{18R_e} \left(\frac{d^2U(R)}{dR^2} \right)_{R=R_e} \quad (5)$$

In determining both the minima and the second derivatives of the potentials, the least squares method was used.

Results and Discussion

The values of R_e , D , and B calculated using the method discussed above are presented in Tables 1-3. The changes made in these values by the inclusion of the next nearest neighbor short-range interaction (2), of the nearest neighbor non-Coulombic long-range force (3), and of both (4), are noted in parentheses. We also provide the available experimental values.

The results show that the inclusion of these often neglected interactions indeed makes small changes in the bond distance and the binding energy of the alkali halide crystals. They are of the order of, but usually less than, 0.1 Å for the bond distances and 10 Kcal/mole for the binding energies. But these are by no means "negligible" numbers. In particular, the values of the bulk modulus, which is far more sensitive to the crystal energy than the other two properties, show much larger variations. The changes do not bring any significant improvement in comparison with the experimental values. This comparison may not be meaningful, however, because the Electron Gas model crystal interaction energy that we have chosen for U_i in Eq. (1) contains other sources of error, possibly of similar magnitudes. What is more important are the magnitudes of the changes. They show that we can not neglect these interactions in any treatment of the alkali halide crystals that aims at an accuracy better than the above sort.

The changes also show some consistent trends. For most of the systems the next nearest neighbor short-range forces shorten the bond distances and increase the binding energies. On the other hand, the non-Coulombic long-range interactions cause the bond distances to increase thereby decreasing the binding energies. The effect of these interactions on the bulk moduli fails to show such a clear trend.

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Photophysical Properties of 1,3-Dimethylnaphtho[1,2-e]uracil

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The solvent change and salt do not affect the fluorescence quantum yield of 1,3-dimethylnaphtho[1,2-e]uracil indicating the considerable energy gap between the lowest singlet (π, π^*) and (n, π^*) states in the compound. The results are consistent with the strong quenching of fluorescence by ethyl iodide. Fluorescence quantum yield is nearly independent of temperature, probably due to the relatively inefficient internal conversion. Unusual spectral difference is observed in isopentane and ethanol at 77K. The temperature dependence of emission in isopentane and in ethanol suggests that the increase of charge transfer character by the conformational change in isopentane leads to the structureless and red-shifted fluorescence, while in ethanol the decrease of the charge transfer character by the hydrogen bonding interaction results in the structured and blue-shifted fluorescence along with phosphorescence at the low temperature. Temperature dependence of emission in poly (methylmethacrylate) matrix indicates that $T_1 \rightarrow S_0$ radiationless decay is an important process responsible for the strong temperature dependence of phosphorescence.

Introduction

Many photophysical and photochemical studies for the heterocyclic compounds have served to emphasize the important role of the (n, π^*) state in the efficient radiationless decay compared with parent aromatic hydrocarbons.¹⁻³ It is now

strongly suspected that an increase in Frank-Condon vibrational overlap factor by the vibronic interaction between the lowest energy (π, π^*) and (n, π^*) singlet states leads to an efficient $S_1 \rightarrow S_0$ internal conversion for many nitrogen heterocyclic and aromatic carbonyl compounds in the condensed phase.⁴

We previously observed that (n, π^*) state gives significant

contribution to the decay from the excited singlet state in an aromatic amide, 5(E)-styryl-1, 3-dimethyluracil.⁵

It is expected that the relative rigidity in structure of 1,3-dimethylnaphtho[1,2-e]uracil, a fused aromatic amide, compared with 5(E)-styryl-1, 3-dimethyluracil restricts the rotatory radiationless decay. Emission and its temperature dependence of 1,3-dimethylnaphtho[1,2-e]uracil are studied in order to investigate the properties of the excited state.

Experimental Section

Materials. 1,3-Dimethylnaphtho[1,2-e]uracil was prepared by photocyclization reaction⁶ of 5(E)-styryl-1,3-dimethyluracil.⁵ The cyclized product was separated by silica gel column chromatography using ethyl acetate-cyclohexane-chloroform (1/1/2, v/v) as the eluent, and recrystallized from chloroform-ethyl ether. 9,10-Diphenylanthracene (Aldrich) was purified by successive recrystallization from ethanol. The solvents for spectroscopic study were of spectroquality.

Spectroscopic Measurements. UV spectra were recorded on a Cary 17 spectrophotometer. Emission spectra were measured on an Aminco-Bowman spectrophotofluorometer with an Aminco-XY recorder at room temperature and at 77K with modification of cell compartment. A cylindrical chopper having the maximum rotating frequency of 10000rpm with two windows opposite to each other was used to isolate phosphorescence from other emission. The phosphorescence lifetime was measured with this instrument, using a mechanical shutter to cut off the excitation light, in conjunction with a Tektronix 5115 storage oscilloscope. To estimate the temperature dependence of fluorescence, temperature of sample cell was continuously varied from 25°C to about -150°C by flowing cold nitrogen gas and maintained to within $\pm 2^\circ\text{C}$ for recording the spectra. The temperature of sample solution was measured with a copper-constant thermocouple. Recorded emission spectra were corrected for the response characteristics of the photomultiplier tube (IP21, S-4 spectral response) and monochromator of this instrument as a function of wavelength. The corrected spectra subsequently permitted the determination of fluorescence quantum yields and ratios of phosphorescence to fluorescence quantum yields. The fluorescence quantum yields at room temperature were determined relative to 9,10-diphenylanthracene ($\phi_f(298\text{K}) = 1.0$ in cyclohexane) by following relationship:

$$\phi_f^s = \phi_f^r \times \frac{I_s \times A_r \times n_r^2}{I_r \times A_s \times n_s^2}$$

where ϕ_f^s represents fluorescence quantum yield of reference and I_s , I_r and A_s , A_r are areas integrated under fluorescence spectra and absorbance at exciting wavelength of sample and reference, respectively, and n_s , n_r are refractive indices of solvents of reference and sample. In quantum yield determinations, absorbance at excitation wavelength was kept as low as possible, usually below 0.3, in order to minimize errors due to the front surface imprisonment and inner-filter effects. Fluorescence quantum yields at 77K were measured using 9,10-diphenylanthracene ($\phi_f(77\text{K}) = 1.0$ in ethanol) as a reference compound, assuming that the relative values of the optical densities and refractive indices of all the solutions at 77K were the same as at room temperature.⁷ The short-wavelength cut-off filters⁸ were employed on exciting and

emitting paths, respectively, to avoid the interference of scattered light. The ratios of phosphorescence to fluorescence quantum yields were estimated by the following correlation; $\phi_p/\phi_f = (\text{area of phosphorescence}) / (\text{area of fluorescence})$. To observe the phosphorescence in a wide range of temperature, poly(methylmethacrylate) (PMMA) matrix was used. The PMMA samples were prepared by dissolving the slices of PMMA and solute ($\sim 5 \times 10^{-3}M$) in dichloromethane followed by solvent evaporation. The prepared PMMA samples were inserted into the tube of suitable size with the position minimizing the scattering in order to prevent the displacement of samples by pressure of nitrogen gas flow. The luminescence spectra and lifetimes were measured simultaneously at various temperatures ($-2^\circ\text{C} \sim -129^\circ\text{C}$).

Results and Discussion

No significant change of the absorption spectrum of 1,3-dimethylnaphtho[1,2-e]uracil (DNU) was observed by changing solvent polarity except the usual broadening in the polar protic solvents. Absorption maximum of DNU is largely red-shifted relative to that of 5-styryl-1,3-dimethyluracil indicating that S_1-S_0 energy gap in DNU is lower than that of 5-styryl-1,3-dimethyluracil due to the increase of conjugation in DNU with more planar structure.

Quantum yields and maxima of fluorescence of DNU in a variety of solvents at room temperature are shown in Table 1. In nitrogen heterocyclic and aromatic carbonyl compounds with close-lying (π, π^*) and (n, π^*) singlet states, vibronic interaction between these two states leads to an efficient $S_1 \rightarrow S_0$ internal conversion and fluorescence quantum yield is generally low and strongly solvent-dependent.^{1,2,9} As shown in Table 1, fluorescence quantum yield of DNU changes little with changing the solvent polarity and is higher than that of 5(E)-styryl-1,3-dimethyluracil and other heteroaromatics. The result is interpreted in terms of small contribution of (n, π^*) state to the lowest excited singlet state and relatively inefficient internal conversion compared to other heteroaromatic compounds with close-lying (π, π^*) and (n, π^*) states and the relative rigidity in structure restricting the rotatory radiationless decay (e.g., ϕ_f of 5(E)-styryl-1,3-dimethyluracil with relatively flexible geometry is 0.023 in ethanol at room temperature). Fluorescence maxima exhibit the usual polar solvent red-shift which is more pronounced in protic solvents relative to in aprotic solvents, with the broadening generally observable in the polar protic solvents.

Alkali metal salts contribute to a change of the relative posi-

Table 1. Solvent Effect on the Fluorescence of 1,3-Dimethylnaphtho[1,2-e]uracil at Room Temperature with $\lambda_{ex} = 320\text{nm}$

Solvent	ϵ^a	λ_{max}, nm	ϕ
Isopentane	1.84	387,370(sh),403(sh)	0.13
Cyclohexane	2.02	388,372(sh),405(sh)	0.11
Ethyl ether	4.34	390,372(sh),405(sh)	0.11
Chloroform	4.81	395,375(sh)	0.09
Dichloromethane	9.08	395,375(sh)	0.10
Acetonitrile	38.8	394,375	0.11
Ethanol	24.3	405	0.10
Methanol	33.62	405	0.11

^aDielectric constant at 20°C from ref. 11.

tion of the excited energy levels by raising the energy level of ${}^1(n, \pi^*)$ state. Fluorescence intensity of DNU are little affected by the addition of an alkali metal salt, sodium acetate. This result implies that, in spite of raising the energy of (n, π^*) singlet state by added salt, the fluorescent ${}^1(\pi, \pi^*)$ state should be little affected because of the considerable energy gap between the lowest excited (π, π^*) and (n, π^*) singlet states, consistent with the above observations of the relatively strong and solvent-independent fluorescence, in contrast to the heteroaromatic compounds with the small energy gap between the lowest singlet (n, π^*) and (π, π^*) states.

Table 2 represents the heavy atom effect on the fluorescence intensity of DNU in methanol. Fluorescence intensity of DNU is strongly reduced with increasing the concentration of ethyl iodide. Because heavy atom induces the enhanced intersystem crossing in the compounds with the lowest excited (π, π^*) , while the compounds with the lowest excited (n, π^*) state is relatively insensitive to the addition of heavy atom¹⁰, the lowest excited singlet state of DNU is again deduced to be (π, π^*) singlet state.

Fluorescence maxima, fluorescence quantum yield, phosphorescence maxima, phosphorescence quantum yield, and phosphorescence lifetime of DNU at 77K are shown in Table 3 and Figure 1. Different from the strong temperature dependence of fluorescence observed in heteroaromatic compounds, fluorescence quantum yield of DNU is little affected by temperature indicating the inefficient internal conversion. Fluorescence quantum yield in isopentane is slightly higher than in ethanol and fluorescence maximum in isopentane is largely red-shifted and broadened compared to that in ethanol at 77K. Phosphorescence to fluorescence quantum yield ratio at 77K is dramatically reduced with changing the solvent from ethanol to isopentane. Phosphorescence maxima is not significantly influenced by the solvent. As the solvent polarity decreases, phosphorescence lifetime at 77K decreases and still is relatively long in isopentane. When an (n, π^*) triplet

state is the lowest triplet state of a molecule, the phosphorescence is short-lived (typically 10^{-3} sec).¹⁰ On the other hand, when the emission occurs from a (π, π^*) triplet state, phosphorescence lifetime is usually considerably longer (on the order of a second in some cases). Therefore, the lowest triplet state of DNU can be assigned to be the (π, π^*) state. Strong solvent dependence of phosphorescence lifetime may be expected from the significant difference between luminescence of DNU in hydrocarbon solvent and in hydroxyl solvent. In contrast to the broad and structureless fluorescence in ethanol at room temperature, fluorescence at 77K is structured and a little blue-shifted. On the other hand, in isopentane fluorescence shows significant red-shift with disappearance of structure as temperature changes from 298K to 77K. These phenomena can be interpreted by the following explanations. As temperature is lowered and the rigidity of medium increases, the conformation changes toward increasing the planarity of DNU in isopentane. As a result, conjugation between π -orbital in naphthalene moiety and lone pair electron on nitrogen atom in uracil moiety increases and then charge transfer character increases, resulting in the structureless and red-shifted fluorescence in isopentane at low temperature. On the other hand, in ethanol the activation of hydrogen bonding interaction between the lone pair electron on nitrogen atom in uracil moiety and solvent with decreasing temperature may compensate with the conformational change and brings about the decrease of charge transfer character and hence the blue-shifted fluorescence.

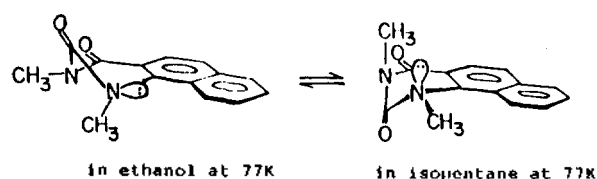


Figure 2 compares the luminescence of DNU in isopentane with that in isopentane containing 2% by volume of ethanol at 77K. When 0.34M ethanol (2% by volume) is added into isopentane solution of DNU, fluorescence is slightly blue-shifted and structured, and phosphorescence appears indicating that hydrogen bonding interaction plays an impor-

Table 2. Heavy Atom Effect on the Fluorescence of DNU in Methanol at Room Temperature

Concentration of Ethyl Iodide, <i>M</i>	I_f^0/I_f^e
0	1.00
0.05	1.08
0.10	1.12
0.25	1.31
0.38	1.50
0.50	1.69

I_f^0 and I_f are the fluorescence intensities in the absence and presence of ethyl iodide, respectively.

Table 3. Fluorescence Maxima (λ_{max}), Fluorescence Quantum Yield (ϕ_f), Phosphorescence Maxima (λ_{max}^p), Phosphorescence Quantum Yield (ϕ_p), and Phosphorescence Lifetime (τ_p) of DNU at 77K with $\lambda_{ex} = 320\text{nm}$

Solvent	λ_{max}, nm	ϕ_f	$\lambda_{max}^p, \text{nm}$	ϕ_p/ϕ_f	τ_p, sec
Isopentane	415	0.17	505, 535	very small	0.87
Ethyl ether	-	-	-	-	1.06
Ethanol	375, 395, 410(sh)	0.12	505, 535, 575(sh)	0.86	1.84

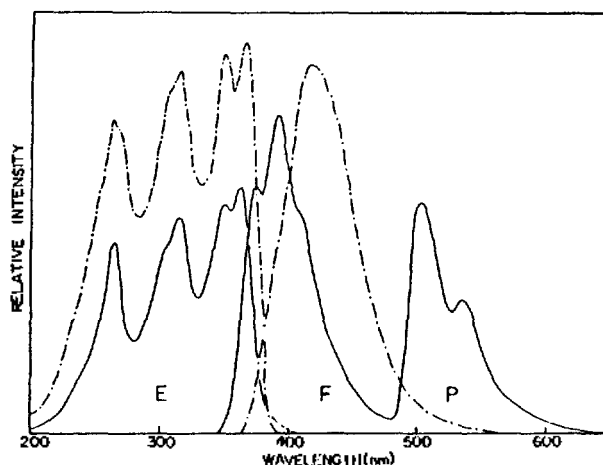


Figure 1. Spectra of DNU in isopentane (—) and ethanol (---) at 77K: E, excitation spectra; F, fluorescence spectra; P, phosphorescence spectra.

tant role for the luminescence of DNU at 77K.

Unusual difference of emission at 298K and 77K is further investigated by study of temperature dependence of emission. Figure 3 shows the temperature dependence (19°C ~ -157°C) of emission of DNU in ethanol. Fluorescence in ethanol at room temperature is broad, structureless. As temperature decreases, fluorescence is slightly blue-shifted and enhanced. Below -92°C, structure of fluorescence appears with large spectral shift and fluorescence quantum yield increases more rapidly than in higher temperature. Below -113°C with maximum fluorescence quantum yield, fluorescence is little shifted and fluorescence quantum yield decreases until the value reaches to the fluorescence quantum yield at 77K ($\phi_f = 0.12$ in ethanol at 77K). This relatively small change in fluorescence quantum yield with temperature especially in higher temperature region is due to inefficient internal conversion because of a large energy gap between $^1(\pi, \pi^*)$ and $^1(n, \pi^*)$ states and rigidity of structure restricting

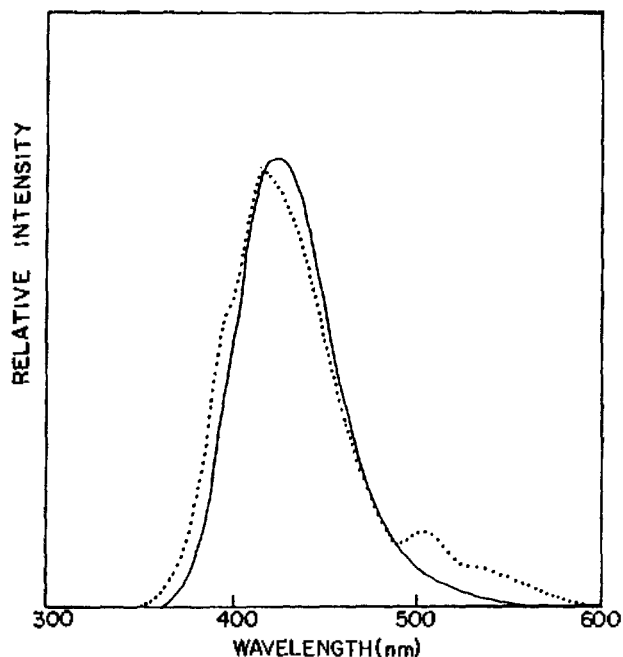


Figure 2. Comparison of emission of DNU in isopentane (—) with that in isopentane containing 2% by volume of ethanol (---) at 77K.

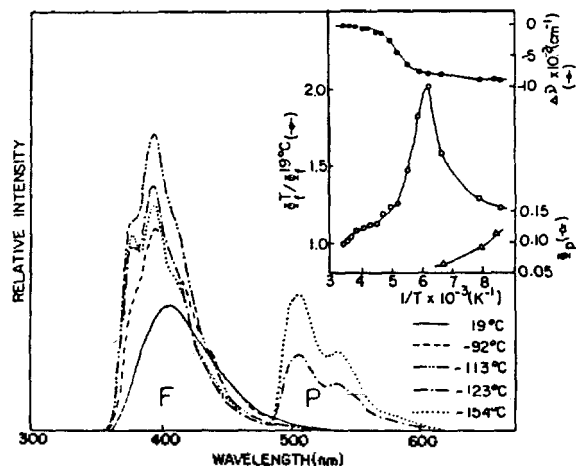


Figure 3. Temperature dependence of emission of DNU in ethanol.

the rotatory radiationless decay. Phosphorescence is observed below -123°C with formation of rigid matrix. Blue-shift of fluorescence of DNU with decreasing temperature may be attributed to the activation of hydrogen bonding interaction between ethanol and nitrogen lone pair electron, resulting in the decrease of charge transfer character by inhibition to the planar structure as described above. Figure 4 shows the temperature dependence (10°C ~ -106°C) of fluorescence of DNU in isopentane. The structured fluorescence of DNU with $\lambda'_{max} = 388\text{nm}$ in isopentane is observed at room temperature. Almost no spectral change is observed until -68°C while the fluorescence quantum yield remained unchanged in the temperature range of 10°C and -44°C. But fluorescence quantum yield is slightly reduced as temperature lowered further. At -80°C, two component fluorescence ($\lambda'_{max} = 390$ and 408nm) appears and the intensity of the second emission component in long wavelength region becomes stronger with decreasing temperature and fluorescence quantum yield shows an minima at this temperature. Below -80°C, structureless and red-shifted fluorescence is observed and fluorescence quantum yield decreases with no spectral change with temperature decrease. Relative insensitivity of fluorescence quantum yield to temperature is again observed as described above. Fluorescence quantum yield at low temperature is not same with that at 77K because the absorbance at room temperature instead of that at 77K was used to calculate the fluorescence quantum yield at 77K. This is confirmed by red-shift of longer wavelength band in excitation spectrum from 358nm at 298K to 365nm at 77K in isopentane. The observed structureless and red-shifted fluorescence in isopentane at low temperature can be explained in terms of the enhanced charge transfer character by the conformational change as described above.

The phosphorescence quantum yield increases with reduction of fluorescence in ethanol raising the question as to whether or not the enhanced $S_1 \rightarrow T_1$ intersystem crossing contributes to the reduction of fluorescence at low temperature. To resolve this problem, poly(methylmethacrylate) matrix is used because phosphorescence can be observed in a wide range of temperature in this matrix. Figure 5 shows the temperature dependence (-2°C ~ -129°C) of fluorescence

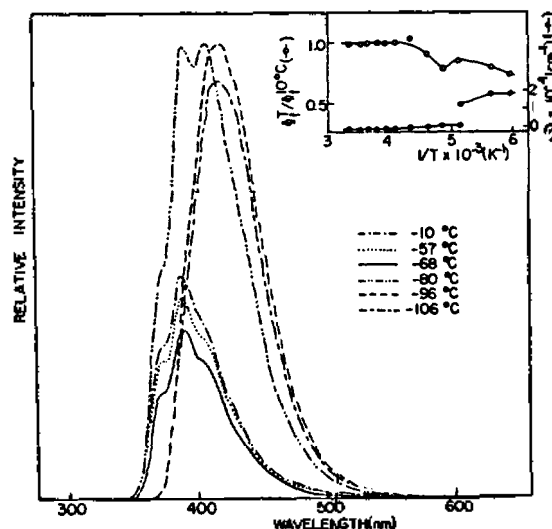


Figure 4. Temperature dependence of fluorescence of DNU in isopentane (sensitivity: -10°C ~ -68°C, 1; -80°C ~ -106°C, 3).

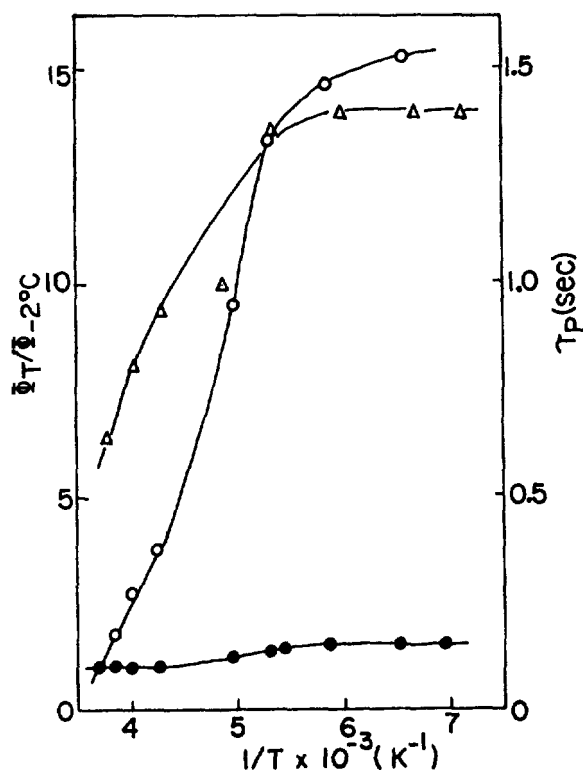


Figure 5. Temperature dependence of Φ_T (●), Φ_p (○), and τ_p (Δ) of DNU in poly(methylmethacrylate) matrix.

quantum yield, phosphorescence quantum yield, and phosphorescence lifetime of DNU in poly(methylmethacrylate) matrix. Fluorescence quantum yield is relatively insensitive to temperature even if very small increase is observed at low temperature, while phosphorescence quantum yield increases sharply with decreasing temperature. If increase of phosphorescence is due to increase of $S_1 \rightarrow T_1$ intersystem crossing rate (k_{isc}), reduction of fluorescence will be concurrently observed but phosphorescence lifetime will be unchanged from equation 1 and 2. However, both quantum yield and

lifetime of phosphorescence sharply increase with decreasing temperature with similar trend in contrast to the unchanged fluorescence quantum yield.

$$\Phi_f = k_f / (k_f + k_{ic} + k_{isc}) \quad (1)$$

$$\Phi_p = k_{isc} / (k_f + k_{ic} + k_{isc}) \times k_p / (k_p + k_{isc}') \quad (2)$$

$$\tau_p = 1 / (k_p + k_{isc}') \quad (3)$$

From equation 2 and 3, this result can be attributed to the decrease of the rate of $T_1 \rightarrow S_0$ radiationless decay (k_{isc}') and this attributes to the strong temperature dependence of phosphorescence because k_p is temperature-independent.

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