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The Phosphorescence Processes in Pyrimidine and 2-Chloropymidine

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The phosphorescence spectra of pyrimidine and 2-chloropyrimidine have been observed at 4.2°K. A detailed vibrational analysis of the pyrimidine spectrum suggests that the emission arises from two components of the emitting triplet state. The phosphorescence lifetimes of pyrimidine and 2-chloropyrimidine have been measured for the 0–0 band and the strongest "vibronic band" (the phosphorescence maximum), which involves various modes of vibrations, at different temperatures between 77 and 1.5°K. The decay curve observed for the 0–0 band has been resolved into two exponential components, and that for the vibronic band, into three exponential components, where the third component was extremely weak in intensity at a very low temperature. From the comparison of the observed and calculated lifetimes of the individual phosphorescence components and their relative intensities, it was deduced that: (1) the 0–0 band involves emissions arising from the B_2 and A_1 components of the $^3B_1(n,\pi^*)$ state, while the vibronic band involves an additional, third emission which very likely arises from the A_2 component; (2) the $^1A_2(n,\pi^*)$ state is located below the $^1B_1(n,\pi^*)$ state; (3) the $^3A_1(\pi,\pi^*)$ state is located below the $^1A_2(n,\pi^*)$ state, and (4) the major intersystem crossing takes place from both the $^1A_2(n,\pi^*)$ and $^1B_1(n,\pi^*)$ states to the $^3A_1(\pi,\pi^*)$ state in pyrimidine and 2-chloropyrimidine.

The phosphorescence spectrum of pyrimidine has been studied by Shimada[1] and by Krishna and Goodman,[2] who assigned the emitting triplet state to a $^3B_1(n,\pi^*)$ state on the basis of vibrational analysis and the solvent effects. Their assignment agreed with the result calculated by Goodman and Harrell.[3] Krishna and Goodman[4] confirmed this assignment by polarization measurements. Furthermore, they[5] calculated the transition probability of the triplet-singlet transition and concluded that

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[1] R. Shimada, *Spectrochim. Acta*, **17**, 30 (1961).

[2] V. G. Krishna and L. Goodman, *J. Amer. Chem. Soc.*, **83**, 2042 (1961).

[3] L. Goodman and R. W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).

[4] V. G. Krishna and L. Goodman, *ibid.*, **36**, 2217 (1962).

[5] L. Goodman and V. G. Krishna, *Rev. Mod. Phys.*, **35**, 541 (1963).

two components can radiatively combine with the ground state in the lowest triplet state of pyrimidine. The same conclusion has, very recently, been obtained by Yonezawa, Katô and Kato.[6] Cohen and Goodman[7] measured the quantum yields of the phosphorescence, fluorescence, internal conversion, and intersystem crossing in pyrimidine and determined the rate constants for these radiative and non-radiative processes. They concluded that the phosphorescence process in pyrimidine is $^1B_1(n,\pi^*) \rightsquigarrow {}^1A_2(n,\pi^*) \rightsquigarrow T(n,\pi^*) \rightarrow {}^1A_1$.[*1]

de Groot, Hesselmann, Schmidt and van der Waals[8] and Hall, Armstrong, Moomaw and El-Sayed[9] studied the phosphorescence decays of quinoxaline and pyrazine respectively and showed that the decay curves of these compounds were non-exponential at very low temperatures ($\sim$1.5°K). The different phosphorescence components, which were analyzed from the decay curves, were ascribed to the transitions from the different sublevels of the lowest triplet state to the ground state. Very recently, Azumi and Nakano[10] measured the phosphorescence lifetime of quinoxaline at various temperatures and estimated the rate constants of the radiative and non-radiative processes from three sublevels of the lowest triplet state to the ground state.

It should be interesting to study the phosphorescence decay of pyrimidine, because the phosphorescence is emitted from two sublevels of the lowest triplet state through first-order perturbation in pyrimidine, while in quinoxaline or pyrazine the phosphorescence is emitted from only one sublevel, and the phosphorescence emitted from two sublevels can provide more information about the phosphorescence processes. This study was undertaken in order to investigate the phosphorescence processes of pyrimidine and 2-chloropyrimidine in more detail through careful analyses of the phosphorescence spectra and decay curves.

Experimental

The pyrimidine was obtained through the reductive dechlorination of trichloropyrimidine with Pd-charcoal.[11] The 2-chloropyrimidine was synthesized with 2-aminopyrimidine, $NaNO_2$, and HCl by means of a diazo reaction.[12] The samples were purified by repeated vacuum distillation just before the experiments.

The phosphorescence spectrum was observed in a methylcyclohexane matrix at 4.2°K with a Hilger spectrograph, type E2. The optical setup and the other apparatus used in this work were the same as those described previously,[13] except that quartz dewars and a thin pyrex sample-cell were used in this case. The 3131 Å Hg-line which was isolated from a 1-kW high-pressure mercury arc lamp, type Orc-CHM-612, with a filter combination of a saturated $NiSO_4$ aqueous solution and a Corning 7-54 glass filter,[14] was used for the excitation of the sample. The necessary exposure time was 24 hr with a slit-width of 25 μ and an Eastman Kodak 103a-O plate. The concentration of the sample was 10^{-4}M.

The lifetime measurement was carried out for each of the 0–0 bands and for one of the vibronic(phosphorescence maximum) bands of the phosphorescence spectrum obtained in methylcyclohexane and benzene matrices at different temperatures between 77 and 1.5°K. The exciting and phosphorescence beams were chopped off with a shutter device designed particularly for this study. The sample was placed between two shutters which were connected with strings and pulleys. First the excitation path was opened and the emission path was closed by a rear shutter so that the excitation could be saturated. Immediately after the excitation path was closed by a front shutter, which was operated by a trigger, the emission path was opened. The two shutters worked so quickly that a short lifetime such as $\sim$5 msec could be determined quite precisely. The lifetime was analyzed with a Bausch & Lomb 500-mm grating monochromator, fixed at a constant wavelength (*e.g.*, the wavelength of the phosphorescence 0–0 band), and with an Iwasaki synchroscope, type SS-5004. The slit-width of the monochromator ranged from 0.5 to 2.5 mm depending on the phosphorescence intensity.

Results

Pyrimidine and 2-chloropyrimidine emit blue phosphorescences in methylcyclohexane and benzene matrices at 4.2°K. The spectra observed at 4.2°K consist of very sharp and highly-resolved bands compared with those observed at 90°K.[1] Their spectral data and microphotometer tracings are given in Table 1 and Fig. 1 respectively.

The decay curves of the phosphorescence lifetimes of pyrimidine and 2-chloropyrimidine, measured for the 0–0 and vibronic bands obtained in methylcyclohexane and benzene matrices at 1.5°K, are shown in Fig. 2. These curves are non-exponential. The curves for the 0–0 bands can be resolved into two components, which give lifetimes of 15 and 58 msec in methylcyclohexane and of 13 and 150 msec in benzene for pyrimidine, and lifetimes of 14

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6) T. Yonezawa, H. Katô and H. Kato, *Theoret. Chim. Acta*, **13**, 125 (1969).

7) B. J. Cohen and L. Goodman, *J. Chem. Phys.*, **46**, 713 (1967).

[*1] $\rightarrow$ and $\rightsquigarrow$denote radiative and non-radiative processes respectively.

8) M. S. de Groot, I. A. M. Hesselmann and J. H. van der Waals, *Mol. Phys.*, **12**, 259 (1967); M. S. de Groot, I. A. M. Hesselmann, J. Schmidt and J. H. van der Waals, *ibid.*, **15**, 17 (1968).

9) L. Hall, A. Armstrong, W. Moomaw and M. A. El-Sayed, *J. Chem. Phys.*, **48**, 1395 (1968).

10) T. Azumi and Y. Nakano, *ibid.*, **50**, 539 (1969).

11) N. Whittaker, *J. Chem. Soc.*, 1646 (1953).

12) "Organic Synthesis," Coll. Vol. IV (1963), p. 182.

13) A. Nakahara, M. Koyanagi and Y. Kanda, *J. Chem. Phys.*, **50**, 552 (1969).

14) M. Kasha, *J. Opt. Soc. Amer.*, **38**, 929 (1948).

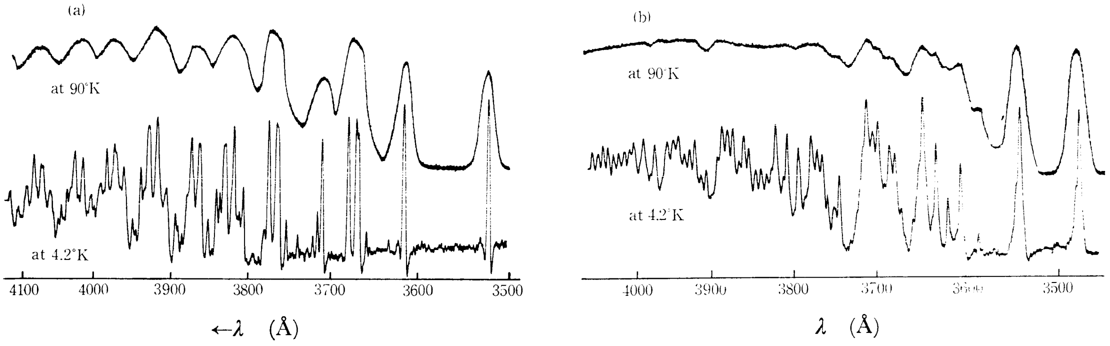

Fig. 1. The phosphorescence spectra of (a) pyrimidine and (b) 2-chloropyrimidine observed in methylcyclohexane at 90 and 4.2°K.

Table 1. Vibrational analysis of the phosphorescence spectrum of pyrimidine in methylcyclohexane at 4.2°K

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment	Symmetry species
28214 vs	0	0, 0	
27816 vw	398	0, 394	a_2
27535 vs	679	0, 677	a_1
27498 vw	716	0, 719	b_1
27412 vw	802	0, 804	b_1
27225 w	989	0, 993	a_1
27161 s	1053	0, 344+719 } Fermi-resonance	a_1
27143 s	1071	0, 1068	a_1
27082 s	1132	0, 1138	a_1
26862 s	1352	0, 677×2	a_1
26812 m	1402	0, 1402	a_1
26771 w	1443	0, 719×2	a_1
26727 vw	1486	0, 677+804	b_1
26643 w	1571	0, 1570	a_1
26539 m	1675	0, 677+993	a_1
26475 s	1738	0, 677+(344+719) } F.r.	a_1
26463 s	1751	0, 677+1068	a_1
26397 s	1817	0, 677+1138	a_1
26356 vw	1858	0, 719+1138	b_1
26175 m	2039	0, 677×3	a_1
26135 w	2079	0, 677+1402	a_1
26087 s	2127	0, 1068×2	a_1
26068 vw	2146	0, 1075×2	a_1
26018 s	2196	0, (344+719)+1138 } F.r.	a_1
26006 s	2208	0, 1068+1138	a_1
25970 m	2244	0, 677+1570	a_1
25938 m	2276	0, 1138×2	a_1

s: strong, m: medium, w: weak, v: very.

and 56 msec in methylcyclohexane and of 30 and 178 msec in benzene for 2-chloropyrimidine. The decay curves for the vibronic bands contain a third, very weak component in addition to the above two. This gives a lifetime of 160 msec in methylcyclohexane and one of 200 msec in benzene for pyrimidine. The intensity of this third component was too weak for it to be analyzed for 2-chloropyrimidine.

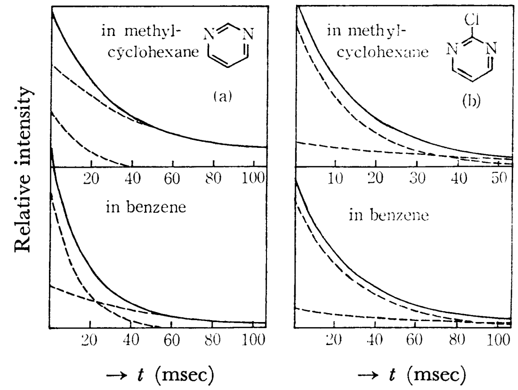

Fig. 2. The phosphorescence decay curves of (a) pyrimidine and (b) 2-chloropyrimidine observed in methylcyclohexane and benzene at 1.5°K —, and analyzed exponential decay curves ----.

We will hereafter call these three lifetime components "short-", "medium-" and "long-lifetime components".

In pyrimidine, the phosphorescence intensity of the medium-lifetime component, which was estimated through the extrapolation of the analyzed exponential curve to $t=0$, is stronger than that of the short-lifetime component in methylcyclohexane, while the former is slightly weaker than the latter in benzene at 1.5°K. In 2-chloropyrimidine, the intensity of the short-lifetime component is stronger than that of the medium-lifetime component in both matrices at 1.5°K. The long lifetime component is very weak in intensity in both matrices. The short-lifetime components increase their intensities with an increase in the temperature for both molecules.

The medium-lifetime component shows a characteristic temperature dependence. The lifetime remains almost constant at temperatures ranging from 1.5 to about 4.2°K. Above 4.2°K, the lifetime begins to decrease with an increase in the temperature, and then it again comes to show a constant value from about 30°K. The values of the lifetime measured in methylcyclohexane at various temperatures are given in Table 2.

The phosphorescence decay curves of the 0–0 and vibronic bands observed at 77°K for both molecules were practically exponential in both matrices. The lifetimes were found to be 27 and 26msec in methylcyclohexane and 29 and 93msec in benzene for pyrimidine and 2-chloropyrimidine respectively. These values are the same as those of the medium-lifetime components measured at 30°K.

Table 2. The lifetimes of the medium components of the phosphorescences of pyrimidine and 2-chloropyrimidine measured in methylcyclohexane at various temperatures

T (°K)		1.5	4.2	7	9	15	27	35	77
τ (msec)	Pyrimidine	58	58	40	37	33	31	27	27
	2-Choloropyrimidine	56	56	—	35	32	—	28	26

Discussion

Vibrational Analysis of the Phosphorescenc Spectrum of Pyrimidine.

The Raman and infrared spectra of pyrimidine have been studied by many workers,[15–18] but the assignments they have given for the fundamental vibrational frequencies do not entirely agree with each other. We will use here the fundamental frequencies given by Sbrana, Adembri, and Califano[17] because their assignments seem to be the most reliable. We will use the same coordinate orientation as that used by Lord, Marston, and Miller;[15] that is, the x axis is perpendicular to the plane of the molecule, and the z axis, along the C_2 axis.

The vibrational analysis of the phosphorescence spectrum observed at 4.2°K is essentially the same as that observed at 90°K,[1] except that the highly-resolved fine structure obtained at 4.2°K enables us to carry out the vibrational analysis in much more detail.

A band at 24214 cm^{-1}, highest in wave number and strongest in intensity, was taken to be the 0–0 band of the spectrum. The very strong bands, which are separated by 679, 1053, 1071 and 1132 cm^{-1} from the 0–0 band, were assigned to the totally symmetric vibrations ν_{6a}, $\nu_{16b}+\nu_{10b}$, ν_{12}, and ν_{9a}*[2] respectively. The splitting of the ν_{12} band and the $\nu_{16b}+\nu_{10b}$ band, which is intensified by the Fermi-resonance, is quite remarkable. The rather weak bands separated by 989, 1402, and 1571 cm^{-1} from the 0–0 band were assigned to the ν_1, ν_{19a}, and ν_{8a} totally symmetric vibrations respectively. All the other prominent bands were assigned to combinations and overtones of these totally symmetric vibrations.

Several extremely weak bands, separated by 398, 716, and 802 cm^{-1} from the 0–0 band, were observed between the 0–0 and 1132 bands. These frequencies may be assigned to three nontotally symmetric vibrations, ν_{16a}, ν_{10b}, and ν_{11} respectively, on the basis of their intensities and frequencies. The first belongs to the a_2 species, and the latter two, to the b_1 species. These vibrations also appear as overtones and combinations with the ν_{6a} and ν_{9a} vibrations in the longer-wavelength region. The detailes of the vibrational analysis are summarized in Table 1.

The degrees of the polarization of the ${}^3B_1(n,\pi^*)\rightarrow{}^1A_1$ phosphorescence relative to excitation into the ${}^1B_1(n,\pi^*)$ and ${}^1B_2(\pi,\pi^*)$ states were observed by Krishna and Goodman to be -0.25 and $+0.15$ respectively.[4] These values are about 75 and 30% of the expected values of -0.33 and $+0.5$ for the angles of $\theta=90°$*[3] and 0° respectively. Although their values were not at the ideal limits, these results clearly indicate that the transition moment of the ${}^3B_1\rightarrow{}^1A_1$ phosphorescence is not completly along the y axis, but partially along the z axis.

Our vibrational analysis of the phosphorescence spectrum also supports this finding. The observation of the a_2 and b_1 vibrations suggests that there are at least two emitting components in the ${}^3B_1(n,\pi^*)$ state. The transitions to the a_2 and b_1 vibrational levels in the ground state can proceed from the B_2 and A_1 components of the ${}^3B_1(n,\pi^*)$ state respectively by borrowing intensities from the electronically-allowed ${}^1B_1(n,\pi^*)$–${}^1A_1$ transition through second-order spin-orbit-vibronic interaction. The emission from the A_2 component is negligibly weak because of the vanishingly small matrix element of the spin-orbit interaction between the ${}^1A_2(n,\pi^*)$ and ${}^3B_1(n,\pi^*)$ states.

The absorption and phosphorescence spectra of 2-chloropyrimidine very closely resemble those of pyrimidine. Polarization measurements of the phosphorescence relative to the absorptions indicate that these two molecules have quite similar electronic structures.[19] Some nontotally symmetric vibrations were also observed in the phosphorescence spectrum of 2-chloropyrimidine. A detailed vibrational analysis of this molecule will be published soon.

Lifetime of the Phosphorescence. The decay

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[15] R. C. Lord, A. L. Marston and F. A. Miller, *Spectrochim. Acta*, **9**, 113 (1957).

[16] V. I. Berezin and S. K. Potapov, *Opt. Spectry.*, **18**, 22 (1965).

[17] G. Sbrana, G. Adembri and S. Califano, *Spectrochim. Acta*, **22**, 1831 (1966).

[18] K. K. Innes, J. P. Byrne and I. G. Ross, *J. Mol. Spectry.*, **22**, 125 (1967).

*[2] The notations given for the fundamental modes are the same as those used by Lord, Marston and Miller.[15]

*[3] θ is the angle between the transition moments of absorption and emission.

[19] N. Nishi, R. Shimada and Y. Kanda, Preprints for the 21st Annual Meeting of the Chemical Society of Japan (April, 1968), I, p. 244.

curve of the 0–0 band of the phosphorescence observed below 4.2°K consists of two exponential components. Above 4.2°K the lifetime of the medium component shortens with an increase in the temperature. This may indicate that below 4.2°K the spin-lattice relaxation process between the triplet state multiplets is slower than both the triplet→triplet internal conversion process and the triplet→ground state radiative process. Hence spin-polarization is nearly preserved, while above 4.2°K the spin-lattice relaxation takes place and the deactivation of the triplet-state-energy *via* a triplet component, from which the phosphorescence is emitted with a short lifetime, gradually increases. This also explains the increase in the intensity of the short-lifetime component with an increase in the temperature. When the temperature goes up above 30°K, the spin-lattice relaxation process fully exceeds other processes and the deactivation of the triplet-state-energy comes approximately to obey the following expression,

$$\tau \approx \frac{3}{k_{qx}+k_{py}+k_{qy}+k_{pz}+k_{qz}} \approx \frac{3}{k_{py}+k_{pz}} = \frac{3}{\dfrac{1}{\tau_{py}}+\dfrac{1}{\tau_{pz}}}$$

where k_p and k_q are radiative and non-radiative rate constants respectively, and where x, y, and z are the indices of the three components of the triplet state.

If the lifetime values of pyrimidine and 2-chloropyrimidine observed in benzene at 1.5°K are substituted into this expression, one obtains 36 and 75 msec respectively. These values approximately agree with those observed at 77°K within the limit of experimental error. If the values observed in methylcyclohexane are substituted into it, however, the agreement becomes rather poor. This may be mainly due to the fact that the ratio of the lifetime values of the medium component to those of the short component is not sufficiently large in this matrix. Therefore, the short-lifetime component was analyzed to be slightly longer in lifetime than the real one.

The transition probability of the ${}^3B_1(n,\pi^*)$-${}^1A_1$ transition of pyrimidine has been calculated by Goodman and Krishna[5] and by Yonezawa, Katô, and Kato.[6] They have shown that: (1) the ${}^3B_1$-${}^1A_1$ transition borrows its intensity from the electronically-allowed S–S and T–T transitions through the first-order spin-orbit interaction; (2) the transition moment is mainly along the y axis, but partially along the z axis also; (3) the ${}^3B_1 \to {}^1A_1$ phosphorescence polarized along the y axis originates from the B_2 component of the ${}^3B_1(n,\pi^*)$ state and has a lifetime of about 4 msec,[5] and (4) the ${}^3B_1 \to {}^1A_1$ phosphorescence along the z axis originates from the A_1 component and has a lifetime of about 70 msec.[5]

These considerations lead to the conclusion that the short-lifetime component should be ascribed to the ${}^3B_1(n,\pi^*)B_2 \to {}^1A_1$[*4] transition, and the medium-lifetime component, to the ${}^3B_1(n,\pi^*)A_1 \to {}^1A_1$ transition.

The long-lifetime component with an extremely weak intensity that has been observed only in the vibronic bands can perhaps be ascribed to the ${}^3B_1(n,\pi^*)A_2 \to {}^1A_1$ transition, but there is no positive evidence in support of this assignment.

Phosphorescence Process. The splitting of two (n,π^*) states of A_2 and B_1 symmetry species in pyrimidine has been calculated to be 1590 and 275 cm^{-1} in the singlet and triplet states respectively, with the A_2 state below the B_1 state in the singlet and with the opposite order in the triplet state.[20] The ${}^3A_1(\pi,\pi^*)$ state was calculated to be located lower in energy than the ${}^1B_1(n,\pi^*)$ state by about 1.4 eV.[21] On the other hand, the ${}^3B_2(\pi,\pi^*)$ state may be expected by analogy with the low-lying triplet states of benzene to lie above the ${}^1B_1(n,\pi^*)$ state.[21]

Cohen and Goodman[7] have indicated, on the basis of the quantum yields of the radiative and non-radiative processes, that: (1) the rate constants of the ${}^1B_1(n,\pi^*) \to {}^1A_1$, $T_1(n,\pi^*) \to {}^1A_1$, ${}^1B_1(n,\pi^*) \rightsquigarrow {}^1A_2(n,\pi^*)$ and ${}^1B_1$ or ${}^1A_2(n,\pi^*) \rightsquigarrow T$ are 5×10^6, $\sim$50, 9.1×10^8 and $1.2\times10^8\ \text{sec}^{-1}$ respectively; (2) the intersystem crossing proceeds from the ${}^1A_2(n,\pi^*)$ state because the internal conversion has the fastest rate constant, hence, the phosphorescence process in pyrimidine is ${}^1B_1(n,\pi^*) \rightsquigarrow {}^1A_2(n,\pi^*) \rightsquigarrow {}^3B_1(n,\pi^*) \to {}^1A_1$, and (3) the intersystem crossing rates are largely dependent on factors other than the matrix element of the first-order spin-orbit interaction. Their considerations are based on the assumption that the ${}^3A_1(\pi,\pi^*)$ state is located above the ${}^1A_2(n,\pi^*)$ state.

The intersystem crossing which proceeds from the ${}^1A_2(n,\pi^*)$ state to the A_2 component of the ${}^3B_1(n,\pi^*)$ state must take place through the first-order spin-orbit interaction, and that to the B_2 or A_1 component, through the second-order spin-orbit-vibronic interaction. The first-order intersystem crossing between the ${}^1A_2(n,\pi^*)$ and ${}^3B_1(n,\pi^*)$ states must be extremely inefficient because of the vanishingly small values of one- and two-center integrals of the matrix element of the spin-orbit interaction and because of the very small Franck-Condon factor, as has been pointed out by El-Sayed.[22] The second-order intersystem crossing between the ${}^1A_2(n,\pi^*)$ and ${}^3B_1(n,\pi^*)$ states through the intermediate (π,π^*) states is expected to be much less efficient than the first-order intersystem crossing between the $S(\pi,\pi^*)$

[*4] ${}^3B_1(n,\pi^*)B_2$ denotes the B_2 component of the ${}^3B_1(n,\pi^*)$ state.

20) M. A. El-Sayed and G. W. Robinson, *J. Chem. Phys.*, **35**, 1896 (1961).

21) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.*, **A70**, 41 (1957).

22) M. A. El-Sayed, *J. Chem. Phys.*, **36**, 573 (1962).

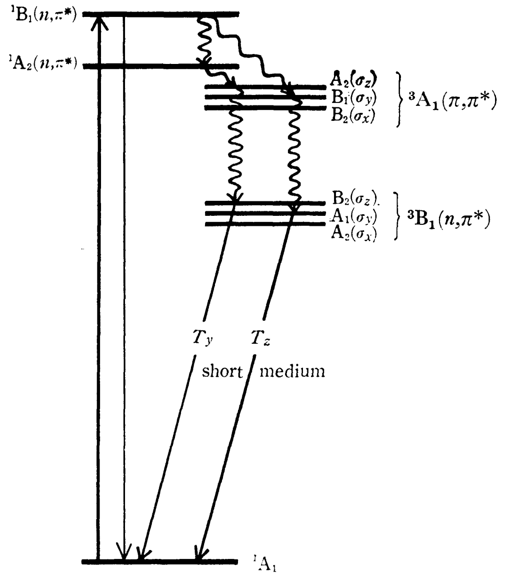

Fig. 3. Phosphorescence processes in pyrimidine and 2-chloropyrimidine.

state of the B_2 or A_1 symmetry and the $^3B_1(n,\pi^*)$ states. In pyrazine, the intersystem crossing proceeds from the $S(n,\pi^*)$ state to the $T(\pi,\pi^*)$ state through the first-order spin-orbit interaction,[7,22] this leads to the strong phosphorescence. Therfore, if Cohen and Goodman's conclusions were correct, pyrimidine should phosphoresce considerably less efficiently than pyrazine. This is, however, contrary to the results of their quantum yield measurements, which show that the rate constant of the intersystem crossing in pyrimidine is smaller than that in pyrazine by a factor of only two.

The observed rather high phosphorescence yield of pyrimidine indicates that the phosphorescence must arise from a non-radiative process, either (1) $^1B_1(n,\pi^*) \rightsquigarrow {}^3A_1(\pi,\pi^*) \rightsquigarrow {}^3B_1(n,\pi^*)$ or (2) $^1A_2(n,\pi^*) \rightsquigarrow {}^3A_1(\pi,\pi^*) \rightsquigarrow {}^3B_1(n,\pi^*)$. The former process requires that the intersystem crossing proceed from the second excited singlet state, while the latter requires that the $^3A_1(\pi,\pi^*)$ state lie below the $^1A_2(n,\pi^*)$ state.

The fact that the 0–0 band of the phophorescence spectrum involves two types of emissions, those due to the $^3B_1(n,\pi^*)A_1 \rightarrow {}^1A_1$ and $^3B_1(n,\pi^*)B_2 \rightarrow {}^1A_1$ transitions, at 1.5°K indicates that both the above two requirements are satisfied in pyrimidine, because these emissions must originate from the non-radiative paths of $^1B_1(n,\pi^*) \rightsquigarrow {}^3A_1(\pi,\pi^*)B_1 \rightsquigarrow {}^3B_1(n,\pi^*)A_1$ and $^1B_1(n,\pi^*) \rightsquigarrow {}^1A_2(n,\pi^*) \rightsquigarrow {}^3A_1(\pi,\pi^*)A_2 \rightsquigarrow {}^3B_1(n,\pi^*)B_2$ respectively. The internal conversion processes between triplet states comply with the requirement of the preservation of spin-polarization (see Fig. 3).

The fluorescence spectrum of pyrimidine was first observed by Börresen[23] and by Cohen, Baba and Goodman.[24] It was assigned to the $^1B_1(n,\pi^*) \rightarrow {}^1A_1$ transition by Cohen and Goodman.[7] This assignment was confirmed by the experimental findings[25] that: (1) the 0–0 band of the fluorescence spectrum exactly coincides with the 0–0 band of the $^1B_1(n,\pi^*) \leftarrow {}^1A_1$ absorption spectrum, and (2) the spectral structure of the fluorescence agrees exactly with the hot bands of the absorption. Neither the absorption nor the fluorescence due to the $^1A_2(n,\pi^*)-{}^1A_1$ transition has been observed. The fact that the fluorescence comes from the second excited singlet state supports the idea that the intersystem crossing can proceed from the $^1B_1(n,\pi^*)$ state.

Halosubstitution induces a blue shift for (n,π^*) states and a red shift for (π,π^*) states. An increase in the energy difference between the $^1B_1(n,\pi^*)$ and $^3A_1(\pi,\pi^*)$ states in 2-chloropyrimidine decreases the rate constant of the intersystem crossing between these two states and hence increases the rate constant of the competing internal conversion between the $^1B_1(n,\pi^*)$ and $^1A_2(n,\pi^*)$ states. This results in an increase in the relative intensity of the short-lifetime component in 2-chloropyrimidine, although its overall phosphorescence intensity is weaker in intensity than that of pyrimidine.

In conclusion, our experimental results support the generally-accepted assumption that the $^1A_2(n,\pi^*)$ state is located below the $^1B_1(n,\pi^*)$ state. Further work is now being undertaken to obtain conclusive evidence regarding the order of these two (n,π^*) states.

The authors are grateful to Dr. Hiroko Shimada for her helpful discussions throughout this work.

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23) H. C. Börresen, *Acta Chem. Scand.*, **17**, 921 (1963).

24) B. J. Cohen, H. Baba and L. Goodman, *J. Chem. Phys.*, **43**, 2902 (1965).

25) M. Hirai, N. Nishi, R. Shimada and Y. Kanda, Preprints for the 22nd Annual Meeting of the Chemical Society of Japan (April, 1969), I. p. 101.