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The Polarized Phosphorescence Spectra of Phenazine in a Phenanthrene Crystal

Kasumi IKEGAMI, Naohiko MIKAMI, and Mitsuo ITO
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai

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The polarized phosphorescence spectra of phenazine in phenanthrene was observed at 4.2 K. From the assignments of vibrations that were made on the basis of the results of polarized Raman spectra measurements for the single crystal, it was concluded that the possible mechanisms for the appearance of the vibronically-induced part of the spectrum are the following:

$$\begin{tikzcd}
{}^3\mathrm{B}_{1u}(\pi,\pi^*) \arrow[r, dash, "\text{s. o.}"] & {}^1\mathrm{B}_{3u}(\mathrm{n},\pi^*) \arrow[r, dash, "\text{vib.}"] & {}^1\mathrm{B}_{2u}(\pi,\pi^*)
\end{tikzcd}$$

$$\begin{tikzcd}
 & {}^3\mathrm{B}_{3u}(\mathrm{n},\pi^*) \arrow[dr, dash, "\text{s.o.}"] & \\
{}^3\mathrm{B}_{1u}(\pi,\pi^*) \arrow[ur, dash, "\text{vib}"] \arrow[dr, dash, "\text{s.o.}"'] & & {}^1\mathrm{B}_{1u}(\pi,\pi^*) \\
 & {}^1\mathrm{B}_{3u}(\mathrm{n},\pi^*) \arrow[ur, dash, "\text{vib}"'] &
\end{tikzcd}$$

Furthermore, it has been found that the vibrational modes which give rise to the more intense in-plane polarized bands are out-of-plane ring modes. These results seem to support the regularity found by Lim *et al.*

It is well known that the different vibronic bands associated with the phosphorescence spectra of organic molecules gain the intensity through different routes of spin-orbit and vibronic couplings. In order to determine the coupling routes, it is necessary to know the polarizations of the individual vibronic bands. Interesting contributions along this line have been made by several investigators. However, they have used mainly the method of photoselection, and this method has problems arising from the necessary use of a rigid glass solution—that is, the broadening of the vibronic bands, the restriction of the lowest temperature employed, and so on. These difficulties may be eliminated by polarization measurements for mixed crystals at very low temperatures.

In the present paper, we will report the polarized phosphorescence spectra of phenazine embedded in a single crystal of phenanthrene at 4.2 K. The results obtained were used to determine the possible coupling routes of the individual vibronic bands. The phosphorescence spectra of phenazine have been studied by Pavlopoulos by the method of photoselection.[1] He has associated some vibronic bands with the infrared active u-vibrations. In view of the results obtained here, his assignments should be revised. We also provide additional evidence supporting the regularity found by Lim *et al.* in the perturbing vibrations which appear in the phosphorescence spectra of polycyclic azine.[2]

Experimental

The phenazine was obtained from the Tokyo Kasei Co. and was purified by recrystallization from various solvents and by alumina-column chromatographic extraction. The phenanthrene which was used as a host crystal was treated with maleic anhydride to remove the contaminated anthracene, then it was subjected to extensive zone melting. The

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1) T. G. Pavlopoulos, *J. Chem. Phys.* **51**, 2936 (1969).

2) E. C. Lim, R. Li, and Y. H. Li, *ibid.*, **50**, 4925 (1969).

phenanthrene crystal (3% phenazine concentration) was grown by the Bridgman method. The crystal was cleaved along the ab-plane, and then cut down perpendicular to it.

To measure the phosphorescence spectrum of phenazine in phenanthrene, the crystal was submerged in liquid helium and front-surface excitation of the crystal was provided by a mercury line of 365 nm from a 500 W high-pressure mercury lamp. A Toshiba UV39 glass filter and a 0.25 m Bausch & Lomb monochromator were used to filter to other mercury lines. The phosphorescence was collected in the same direction as that of excitation with a lens on the slit of a 0.75 m Nalumi double-grating monochromator (dispersion, 11A/mm) after having passed through a polarized sheet and a Babine plate. The spectrum was recorded with an EMI 9558BQ multiplier phototube and a photon-counting system.

The polarized Raman spectra of a phenazine single crystal were also measured with the exciting light of 4880Å of an Ar-ion laser and a Nalumi double-grating monochromator.

Results and Discussion

The phosphorescence spectrum of phenazine in a phenanthrene crystal at 4.2 K is shown in Fig. 1. The intense and sharp band at 15787 cm^{-1} is onsidered to be an 0–0 band. The vibrational analysis of the observed bands is shown in Table 1, in which the wave number differences from the 0–0 band are compared with the vibrational frequencies obtained from the Raman spectrum. Pavlopoulos[1)] observed the phosphorescence spectrum of phenazine in *n*-heptane at 77 K and assigned the 0—486, 0—581, 0—761, 0—823 cm^{-1} bands in the phosphorescence spectrum to the 474, 596, 751, and 820 cm^{-1} infrared active u-vibrations respectively. The 0—486, 0—761, and 0—823 cm^{-1} bands in his spectrum correspond to the 0—495, 0—776, and 0—832 cm^{-1} bands in our spectrum; no band corresponding to his 0—581 cm^{-1} band was observed here. As is shown in Table 1, the 0—495 cm^{-1} band is assigned to the Raman line of 494 cm^{-1}, and it is more reasonable to assign the 0—776 and 0—832 cm^{-1} bands to 416+356 cm^{-1} and 416 cm^{-1}×2 respectively. Thus, Pavlopoulos' assignment of some vibronic bands to the infrared active u-vibrations should be revised. It is the Raman active vibrations which are associated with all the vibronic bands in the phosphorescence spectrum of phenazine.

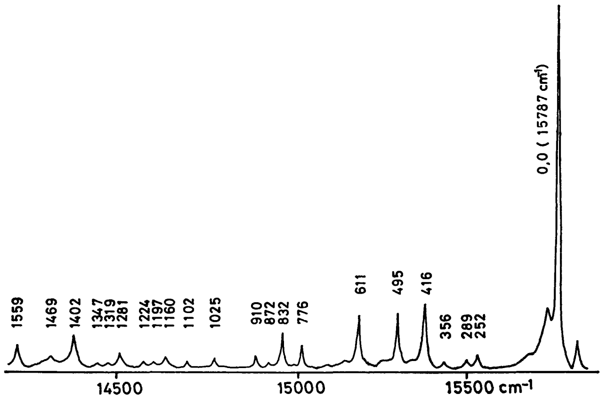

Fig. 1. Phosphorescence spectrum of phenazine in phenanthrene at 4.2 K.

Table 1 also gives the symmetry species of the Raman lines, which were determined from polarization mea-

TABLE 1. VIBRATIONAL ANALYSIS OF THE PHOSPHORESCENCE SPECTRUM OF PHENAZINE IN PHENANTHRENE AT 4.2 K AND RAMAN FREQUENCIES OF PHENAZINE

Phosphorescence (cm^{-1})	Intensity	Difference from the 15787 cm^{-1} band	Assignment	Polarization	Raman frequencies	Symmetry species
15787	vvs	···		N		
15532	w	252	252	L	245	b_{1g}
15498	w	289	289	M	286	b_{2g}
15438	w	356	356	L?	358	
15371	s	416	416	N	415	a_g
15292	s	495	495	L	494	b_{1g}
15176	s	611	611	N	611	a_g
15011	m	776	416+356	L		
14955	m	832	416×2	N		
14915	w	872	611+252	L		
14877	w	910	416+495	L		
14762	w	1025	416+611	N		
14685	w	1102	611+495	L		
14627	m	1160	1160	N	1155	a_g
14590	w	1197	1197	N	1208	a_g
14563	w	1224	611×2	N		
14506	m	1281	1281	N	1278	a_g
14468	w	1319	416×2+495	L		
14440	m	1347	1347	N	1346	a_g
14379	m	1402	1402	N	1400	a_g
14318	w	1469	1469	N	1475	a_g
14228	m	1559	1559	N	1553	a_g

surements for the phenazine single crystal, as well as from depolarization factors for liquid phenazine obtained by melting. As for the nontotally symmetric lines, the Raman line at 494 cm^{-1} can definitely be assigned to the b_{1g} species on the basis of the polarization characteristics of the crystal spectra, while the Raman lines at 245 and 286 cm^{-1} remain ambiguous due to their weak Raman intensities. The latter probably correspond to the 243 and 290 cm^{-1} of anthracene, which belong to b_{1g} and b_{2g} respectively.[3] The 358 cm^{-1} line remains unassigned because of its weak intensity.

In order to determine the polarization directions of individual vibronic bands of the phosphorescence spectrum, the polarized phosphorescence spectra of phenazine were observed for the single crystal of phenanthrene containing 3% phenazine at 4.2 K. The phenanthrene crystal belongs to a monoclinic system with the space group $P2_1$. The bimolecular unit cell has dimensions of $a=12.967$ Å, $b=4.981$ Å, $c=7.056$ Å, and $\beta=109.0°$.[4] Table 2 gives the squared direction cosines of the L, M, and N-axes of the molecule (L, M, and N respersent the long molecular axis, the short molecular axis, and the normal to the molecular plane respectively) with respect to the a, b, and c* axes of the crystal respectively. If we assume that, in the mixed crystal, the phenazine molecules substitutionally occupy the molecular sites of the phenanthrene crystal in such a way that the, L, M, and N axes of the phenazine molecule are parallel to the corresponding axes of the phenanthrene molecule, Table 2 will predict that the vibronic bands of the phosphorescence spectrum of phenazine having transition moments parallel to the L, M, and N-axes should favorably appear along the c*, b, and a-axis spectra respectively. The polarized phosphorescence spectra from the ab and bc* planes are shown in Figs. 2 and 3 respectively. Although the polarization ratios deviate appreciably from the values expected from Table 2 because of the depolarization caused by the cryostat windows, the crystal surface, and so on, the directions of the polarization of the individual vibronic bands may be determined uniquely from Figs. 2 and 3. The 0—0, 0—416, and 0—611 cm^{-1} bands are polarized along the a-axis, so these bands are of the N-axis polarization. The 0—495 and 0—252 cm^{-1} bands are of the L-axis polarization, for these bands appear strongly in the c* axis spectrum. The 289 cm^{-1} band appears strongly along the b axis, and so it is of the M-axis polarization. Similarly, the polarization directions of all the vibronic bands observed were determined; these results are listed in the fifth column of Table 1.

Table 2. Squared direction cosines between the molecular fixed axes L, M, and N and the crystal axes a, b, and c* in phenanthrene crystal

	a	b	c*(⊥ab)
L	0.0648	0.0073	0.9279
M	0.1964	0.7676	0.0386
N	0.7406	0.2251	0.0343

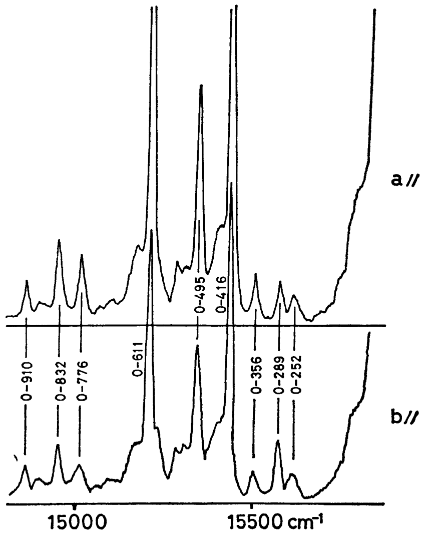

Fig. 2. Polarized phosphorescence spectra of phenazine in phenanthrene (ab face) at 4.2 K.

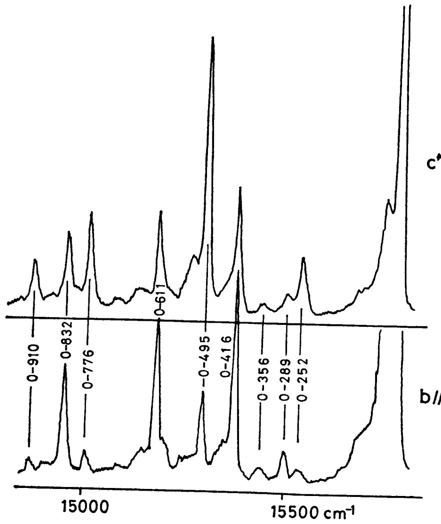

Fig. 3. Polarized phosphorescence spectra of phenazine in phenanthrene (bc* face) at 4.2 K.

To discuss the origin of vibronic bands appearing in the phosphorescence spectrum of phenazine, we need information about the electronic states of phenazine; the information can be obtained from the absorption studies by Mikami[5] and by Hochstrasser[6] for a phenazine single crystal. The crystal spectrum of phenazine has an n-π* absorption at 20800 cm^{-1} and three strong π-π* absorption at about 47600, 40000, and 27800 cm^{-1}. The n-π* absorption at 20800 cm^{-1} is assigned to the symmetry-allowed $^1B_{3u}\leftrightarrow{}^1A_g$ transition. The π-π* absorption at 47600 and 40000 cm^{-1} are attributed, respectively to a $^1B_{1u}\leftrightarrow{}^1A_g$

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[3] M. Suzuki, T. Yokoyama, and M. Ito, *Spectrochim. Acta*, **24A**, 1091 (1968).

[4] J. Trotter, *Acta Crystallogr.* **16**, 605 (1963).

[5] N. Mikami, *J. Mol. Spectry.* **37**, 147 (1971).

[6] R. Hochstrasser, *J. Chem. Phys.* **36**, 1808 (1961).

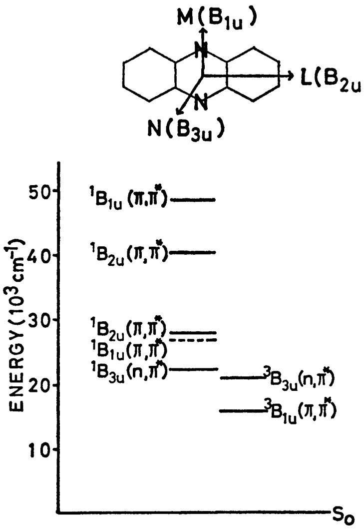

Fig. 4. The low lying singlet and triplet states of phenazine. (The location of the ${}^1B_{1u}$ (π,π^*) state shown by broken lines is not established.)

transition with the transition moment parallel to the short axis of the molecule and to a ${}^1B_{2u}\leftrightarrow{}^1A_g$ transition with the transition moment parallel to the long axis of the molecule. However, there are two alternatives for the assignment of the 27800 cm^{-1} π–π^* absorption; one is the assignment of the ${}^1B_{1u}\leftrightarrow{}^1A_g$ π–π^* transition with the transition moment parallel to the short axis of molecule, and the other is the superposition of two kinds of π–π^* transitions, ${}^1B_{1u}\leftrightarrow{}^1A_g$ and ${}^1B_{2u}\leftrightarrow{}^1A_g$. As for the triplet states, the lowest triplet states is known to be ${}^3B_{1u}(\pi, \pi^*)$. The second triplet state, studied recently by Mikami and Ito,[7] was assigned to ${}^3B_{3u}$ on the basis of the polarized absorption spectra of the single crystal. The low-lying electronic states of phenazine described above are shown in Fig. 4.

Now, we shall discuss the origin of each vibronic band, based on the vibronic spin-orbit interaction scheme. The Hamiltonian involving spin-orbit interaction[8] is written to the first order in nuclear displacement by:

$$\mathbf{H} = \mathbf{H}_o^\circ + \mathbf{H}_{so}^\circ + \sum_a \left\{\left(\frac{\partial \mathbf{H}_o}{\partial \mathbf{Q}_a}\right)^0 + \left(\frac{\partial \mathbf{H}_{so}}{\partial \mathbf{Q}_a}\right)^0\right\}\mathbf{Q}_a$$

where $\mathbf{H}_o{}^\circ$ is an unperturbed term, where $\mathbf{H}_{so}^\circ$ is a spin-orbit coupling operator, and where $\mathbf{Q}_a$ indicates a normal coordinate, the superscript zero referring to the equilibrium nuclear configurations. The vibronic wave function of the triplet state with which we are now concerned is thus written, according to the second-order perturbation theory, by:

$$\begin{aligned} {}^T\theta = {}^T\theta_o &+ \sum_S \frac{\langle S|\mathbf{H}_{so}^\circ|T\rangle}{E_{ST}}\,{}^S\theta_o + \sum_S \frac{\langle S|\mathbf{H}_{so}'|T\rangle}{E_{ST}}\,{}^S\theta_o \\ &+ \sum_S \sum_{S'} \frac{\langle S|\mathbf{H}_o'|S'\rangle}{E_{SS'}}\,\frac{\langle S'|\mathbf{H}_{so}^\circ|T\rangle}{E_{S'T}}\,{}^S\theta_o \\ &+ \sum_S \sum_{T'} \frac{\langle S|\mathbf{H}_{so}^\circ|T'\rangle}{E_{ST'}}\,\frac{\langle T'|\mathbf{H}_o'|T\rangle}{E_{TT'}}\,{}^S\theta_o \end{aligned}$$

where $\mathbf{H}_o'$ and $\mathbf{H}_{so}'$ represent $(\partial\mathbf{H}_o/\partial\mathbf{Q}_a)^\circ\mathbf{Q}_a$ and $(\partial\mathbf{H}_{so}/\partial\mathbf{Q}_a)^\circ\mathbf{Q}_a$ respectively. S′ and T′ indicate intermediate singlet and triplet states. The second term represents a usual spin-orbit coupling for a pure electronic state. The third term represents a "direct spin vibronic coupling". The fourth and last term are called "vibronic coupling in the singlet manifold with spin-orbit coupling" and "spin-orbit coupling with vibronic coupling in the triplet manifold" respectively.

It may be seen from Table 1 that the 0—0 band and the bands involving the totally symmetric vibrations are out-of-plane polarized. Since the lowest triplet state is ${}^3B_{1u}$, these bands borrow their intensities from the ${}^1B_{3u}\leftrightarrow{}^1A_g$ transition through usual spin-orbit coupling. The lowest n–π^* ${}^1B_{3u}$ state is considered to be most responsible for the coupling. This confirms the previous conclusions about the origin of the 0—0 band reached by many workers. As for the origin of the vibronic bands of the in-plane polarizations, that is, the 0—252, 0—289, and 0—495 cm^{-1} bands, we have to consider the spin-orbit coupling in the singlet manifold or triplet manifold (the third or fourth term of the above equation). Since the 0—252 and 0—495 cm^{-1} bands are long-axis polarized, they must borrow their intensity from the ${}^1B_{2u}\leftrightarrow{}^1A_g(\pi, \pi^*)$ transition. There are two low-lying ${}^1B_{2u}$ states in the 27800 and 40000 cm^{-1} regions, but energy considerations suggest that the intensity borrowing from the ${}^1B_{2u}\leftrightarrow{}^1A_g(\pi, \pi^*)$ transition in the 27800 cm^{-1} region contributes mainly to the long-axis polarized vibronic bands. Since the ${}^1B_{2u}(\pi, \pi^*)$ state can not couple effectively with ${}^3B_{1u}(\pi, \pi^*)$ state by means of spin-orbit coupling, and since all the long-axis polarized bands involve the b_{1g} vibrations, the following scheme is considered to be the most likely one:

$${}^3B_{1u}(\pi,\pi^*)\ \underset{R_y}{\overset{\text{s.o.}}{\text{———}}}\ {}^1B_{3u}(n,\pi^*)\ \underset{b_{1g}}{\overset{\text{vib}}{\text{———}}}\ {}^1B_{2u}(\pi,\pi^*)$$

As for the short-axis polarized vibronic band of 0—289 cm^{-1}, it borrwos its intensity from the ${}^1B_{1u}\leftrightarrow{}^1A_g(\pi, \pi^*)$ transition. Either the ${}^1B_{1u}$ state of 47600 cm^{-1} or the ${}^1B_{1u}$ state of 27800 cm^{-1} must be responsible for it. Since the 0—289 cm^{-1} band involves the b_{2g} vibration, the most likely coupling routes are:

$${}^3B_{1u}(\pi,\pi^*)\ \underset{b_{2g}}{\overset{\text{vib}}{\text{———}}}\ {}^3B_{3u}(n,\pi^*)\ \underset{R_y}{\overset{\text{s.o.}}{\text{———}}}\ {}^1B_{1u}(\pi,\pi^*)$$

$${}^3B_{1u}(\pi,\pi^*)\ \underset{R_y}{\overset{\text{s.o.}}{\text{———}}}\ {}^1B_{3u}(n,\pi^*)\ \underset{b_{2g}}{\overset{\text{vib}}{\text{———}}}\ {}^1B_{1u}(\pi,\pi^*)$$

It is interesting to note here that all three schemes given above contain vibronic coupling between n–π^* and π–π^* states. Vibronic coupling between n–π^* and π–π^* states is realized only through and out-of-plane vibration. In the study of the perturbing vibrations of the phosphorescence spectra of polycyclic azines, Lim *et al.*[2] showed that the out-of-plane hydrogen wagging vibration of the CH group adjacent to the heteroatoms is responsible for the appearance of relatively strong in-plane polarized vibronic bands in the π–π^* phosphorescence of dibenzo (*f*, *h*) quinoxaline, while, in dibenzo (*a*, *c*) phenazine, where there is no CH group adjacent to the nitrogen atoms, the

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7) N. Mikami, and M. Ito, This Bulletin **45**, 992 (1972)

8) A. C. Albrecht, *J. Chem. Phys.* **38**, 354 (1963).

vibrational modes which give rise to the more intense in-plane polarized vibronic bands are of the out-of-plane ring mode. In the case of phenazine, where there is no CH group adjacent to the nitrogen atoms, the out-of-plane ring mode should be active if the regularity found by Lim *et al.* applies in our case also. The active fundamental vibrations in the phosphorescence spectrum of phenazine are of frequencies less than 500 cm^{-1}. Therefore, they are not due to the CH vibration (their frequencies are too low), but are probably due to the out-of-plane ring mode. In our recent study of the polarized phosphorescence spectra of quinoxaline, phthalazine, and quinoline, whose molecules have the CH group adjacent to the nitrogen atoms, we found that the out-of-plane CH bending vibrations (872 cm^{-1} of quinoxaline and 921 cm^{-1} of phthalazine)[9] are active vibrations in the phosphorescence spectra. These facts seem to support the regularity found by Lim *et al.* for the perturbing vibrations in the phosphorescence spectra of polycyclic azines.

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9) K. Ikegami and M. Ito, unpublished result.