On the Origin of Differences in the Phosphorescence Band Patterns of *p*-Benzoquinone in *p*-Dihalobenzene Crystals[1)]

Yusei Miyagi, Motohiko Koyanagi,* and Yoshiya Kanda

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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The phosphorescence spectra of *p*-benzoquinone (PBQ) have been studied at 4.2 K in isostructural crystals such as *p*-dichlorobenzene (DCB), *p*-bromochlorobenzene (BCB), and *p*-dibromobenzene (DBB); and in their binary mixed crystals. The variable phosphorescence band patterns observed are interpreted in terms of anisotropic local-field effects of the host environmental molecules. A similarity of the phosphorescence intensity distribution between two systems of PBQ/BCB and PBQ/(0.5 molar fraction of DCB+0.5 molar fraction of DBB) is a manifestation of the existence of effective local-fields in the crystals.

Extensive spectroscopic studies have been carried out on the lowest excited triplet state of *p*-benzoquinone (hereafter abbreviated as PBQ) in rigid matrices[2-9)] and have served as the basis for understanding emission spectra of more complex quinoidal compounds, *e.g.*, the emission spectra of 9,10-anthraquinone[10-12)] and 1,4-naphthoquinone.[13)] No widely accepted theoretical work on the energy splitting $\Delta E(n_+ - n_-)$ has appeared so far despite a great interest in knowledge about the extent of interaction between the two zeroth order n orbitals on the two carbonyl oxygens. The energy separation between the two $n\pi^*$ states of the same spin-multiplicity, which originate mainly in the $\pi_5 \leftarrow n_+$ and $\pi_5 \leftarrow n_-$ excitations, is also controversial.[14,15)]

The phosphorescence is expected sensitive even to a feasible perturbation because PBQ has a small energy gap between $T_1(n_-\pi_5^*)$ and $T_2(n_+\pi_5^*)$ states, *e.g.*, 0.002—0.04 eV depending on environments.[3-9,14)] The perturbation may be external (*e.g.*, environmental), or internal (*e.g.*, vibrational), or a combination of both. The objectives of this paper are to examine a change in the phosphorescence spectral pattern of PBQ with a change in environmental force-fields and to demonstrate a great dependence of the PBQ spectral pattern upon environments.

Experimental

All chemicals of extra pure grade were obtained from Tokyo Kasei Co. Ltd. The guest substance PBQ was recrystallized at least twice from petroleum ether prior to several vacuum sublimations. All the host substances, *i.e.*, *p*-dibromobenzene (abbreviated as DBB), *p*-dichlorobenzene (DCB) and *p*-bromochlorobenzene (BCB), were sublimed *in vacuo* and then zone-refined more than 70 passes. The guest concentration of about 10^{-3} in mol/mol ratios was generally employed. All mixed crystals were grown using the usual Bridgman method. The apparatus and experimental conditions are similar to those described previously.[16)] No intensity correction was carried out for photomultiplier response, grating reflection property, and quantum efficiency difference because the locations of the phosphorescence origin bands in the three matrices are close to each other and only their relative intensities are referred to in this paper.

Crystal Structure of DBB, DCB, and BCB

All hosts have well been known to crystallize in the same space group of $C_{2h}^5(P2_{1/a})$ with two molecules in the unit cell and to have nearly identical unit cell dimensions.[17-19)] The representative crystal structure of these hosts is shown in Fig. 1 and the dimensional data cited are given in Table 1. If a mixed crystal is grown very slowly from the melt mixed with two types of these *p*-dihalobenzenes, each lattice point of the mixed crystal can be regarded as a statistical average of the two types of molecules.[20)] As for the BCB crystal itself, the halogen positions are filled at random by bromine or chlorine.[19,21)] Since the space group has four general positions, only a statistical symmetry is possible with a center of symmetry at the center of the average molecule. Its benzene ring is assumed as a regular hexagon of 1.41 Å in side and the C–X (halogen) bond lengths of 1.77 Å are intermediate between C–Cl (1.69 Å in DCB) and C–Br (1.88 Å in DBB).[19,22)] The permanent diplole moment of BCB has been reported to be 0.1 D.[23)] This is very close to an estimated value of 10^{-1} D from a vector combination of the dipole moments available for chlorobenzene and bromobenzene.[24)]

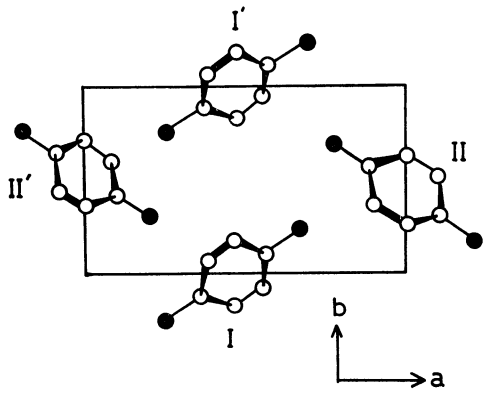

Fig. 1. Crystal structure of DCB and DBB (after Croatto *et al.*, Ref. 17).
●: Br or Cl, ○: C.

Table 1. The dimensional parameters of the crystals of DCB, BCB, and DBB

	DCB[a)]	BCB[b)]	DBB[c)]
a/Å	14.80	15.20	15.36
b/Å	5.78	5.86	5.75
c/Å	3.99	4.11	4.10
β	113°00′	113°12′	112°38′

a) Data taken from Ref. 18. b) Data taken from Ref. 19. c) Data taken from Ref. 17.

Results

Phosphorescence Spectra. The phosphorescence spectra of PBQ in BCB, DCB, and DBB at 4.2 K are shown in Fig. 2. Here two characteristic bands are designated as *a* and *q*. The band *a* lying at the shortest wavelength of the emission systems contains the origin band and the band *q* both the ν(C=O) symmetric and antisymmetric vibrational bands. At a glance the phosphorescence band pattern of PBQ/BCB resembles that of the $^3B_{1g}\rightarrow{}^1A_g$ phosphorescence of PBQ/toluquinone reported previously.[9] On the other hand, the spectra of PBQ/DCB and PBQ/DBB are of the "forbidden-type" spectral pattern whose features have been discussed somewhat minutely in the phosphorescence spectrum of PBQ/naphthalene.[9] The phosphorescence spectrum of PBQ/DCB resembles those reported previously.[2,3] However, all the spectra of this system seem to contain additional emission components with broad band feature. Such additional emissions have also been reported for other guest molecules in the same DCB host and attributed to different phases of the host crystal.[25,26] Except the band broadness, the spectral intensity distribution of PBQ/DCB is rather close to that of PBQ/DBB. The strongest band in both systems is ascribed to the ν(C=O) antisymmetric b_{1u} vibrational mode.[2,3,6-8]

Another intensity aspect is given through a study on the phosphorescence spectra of PBQ in a binary-component crystal system, *i.e.*, PBQ/(DCB–DBB). In Fig. 3 are shown the phosphorescence spectra of PBQ at various molar fractions of DCB in DBB. For convenience' sake, all the emission spectra were roughly normalized in the peak height of the band *q* around 16750 cm^{-1}. Obviously the band *a* increases in intensity, relative to the intensity of the band *q*, with an increase in DCB molar fraction x_{DCB} from 0 to 0.5. A similar concentration dependence was also observed with an increase in DBB concentration x_{DBB} from 0 to 0.5. It should be noted that the phosphorescence band pattern at $x_{DCB}=x_{DBB}=0.5$ is very similar to that of PBQ/BCB (compare the spectral curve (6) in Fig. 3 with that given in Fig. 2a).

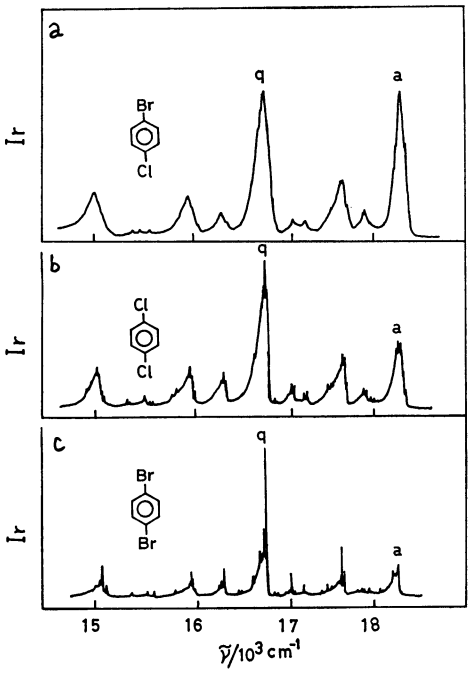

Fig. 2. Phosphorescence spectra of PBQ in (a) BCB, (b) DCB, and (c) DBB at 4.2 K. An apparent band *a* represents the origin band region containing some phonon modes and *q* the ν(C=O) band region. The ordinate I_r means a relative output signal intensity. No intensity correction is given in this Figure.

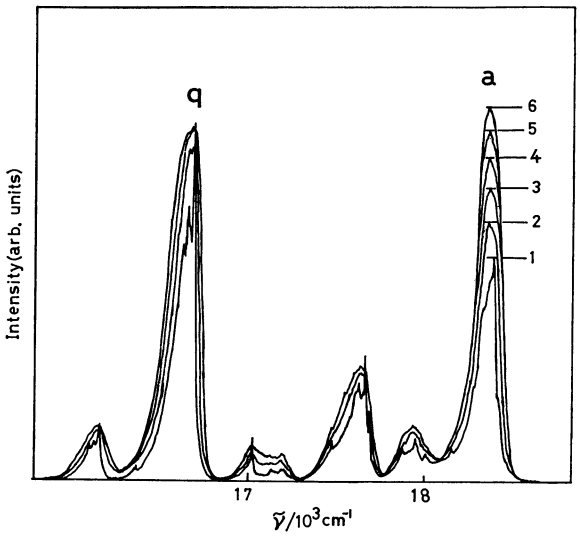

Fig. 3. Phosphorescence spectra of PBQ in binary host crystals of DCB/DBB at 4.2 K. The guest concentration is almost constant, *i.e.*, $\approx 10^{-3}$ mol/mol. The molar fractions of DCB in DBB are (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.3, (5), 0.4, and (6) 0.5. To avoid the confusion of band overlappings, we employ a suitable abbreviation in this Figure.

Intensity Correlation in Binary Host Crystals. A meaningful correlation is obtained between the intensity increment of the apparent band *a* and the molar fraction of x_{DCB} (hereafter abbreviated simply as *x* unless noted especially) in the binary host system, *i.e.*, DCB/DBB. Since estimation of the absolute intensity of emission spectra is generally difficult, we take only a relative intensity. The intensity of the band *a* may approximately be represented as

$$\int_{\tilde{\nu}_a-\Delta}^{\tilde{\nu}_a+\Delta} f(\tilde{\nu}, x)\,d\tilde{\nu} = F_a(x), \tag{1}$$

where $f(\tilde{\nu},x)$ is the uncorrected shape-function of the observed phosphorescence spectrum at a solvent constituent *x* and Δ is taken as a region much greater than any *hwhm* in all mixed crystal systems but less than 400 cm^{-1} since a next prominent band might usually appear around 400 cm^{-1} region from the band in question and we must exclude such an unnecessary component from the intensity estimation. Similarly the intensity of the band *q* is given by

$$\int_{\tilde{\nu}_q-\Delta}^{\tilde{\nu}_q+\Delta} f(\tilde{\nu}, x)\,d\tilde{\nu} = F_q(x). \tag{2}$$

Since these bands are extremely strong in intensity and the intensities of other bands as combination

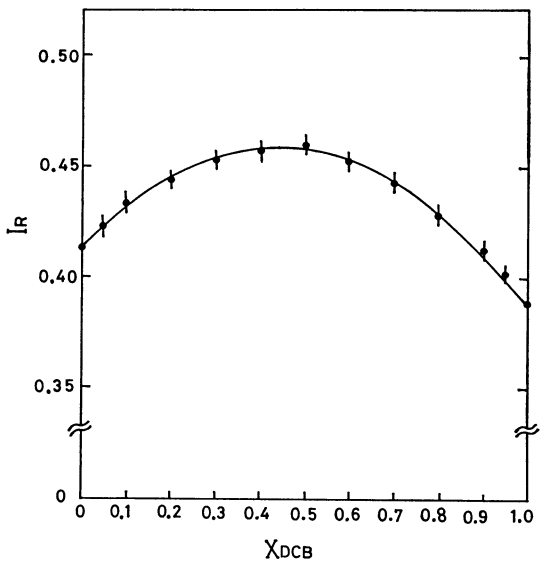

Fig. 4. A correlation between the relative intensity of the "origin" band, I_R, and the concentration of DCB in the binary host system of DCB–DBB, x. ●: Observed value, —: simulated parabola (the analytical details are given in the article).

bands are closely related to either the origin band or the false origin band, it will be reasonable to employ an approximate relative intensity of the band a as follows:

$$I_R(x) = F_a(x)/\{F_a(x)+F_q(x)\}. \quad (3)$$

The observed values of I_R against x are plotted in Fig. 4. An analytical expression for the empirical plot is given by

$$I_R(x) = -0.236x^2 + 0.212x + 0.413. \quad (4)$$

The solid curve in Fig. 4 shows this parabola.

Theoretical Consideration

General Spectral Behaviors in a Binary A–B Host System. Now let us assume that a guest molecule is surrounded by n solvent molecules. Each solvent site is occupied by either an A or a B molecule. It is, of course, statistical which molecule of them takes a certain site i. There are $N(=2^n)$ arrangements of the binary host molecules unless any symmetrical simplification is taken into account. In general the observed shape function $f(\tilde{\nu}, x)$ is represented as the arithmetic mean over all these arrangements:[27]

$$f(\tilde{\nu}, x) = \frac{1}{N}\sum_{R}^{N} f_R(\tilde{\nu}, x). \quad (5)$$

Here $f_R(\tilde{\nu}, x)$ denotes the shape function of a certain host arrangement R and is developed in terms of the binomial distribution function with two parameters n and m:

$$f_R(\tilde{\nu}, x) = \sum_m \binom{n}{m} x_A^n x_B^{n-m} f^\circ_{mR}(\tilde{\nu}), \quad (6)$$

where $f^\circ_{mR}(\tilde{\nu})$ signifies the shape function of the arrangement R with m sites of the A molecule and n-m sites of the B molecule. The actual emission shape is thus developed as a polynomial of x with degree n:

$$f(\tilde{\nu}, x) = K_n(\tilde{\nu})x^n + K_{n-1}(\tilde{\nu})x^{n-1} + \cdots + K_1(\tilde{\nu})x + K_0(\tilde{\nu}). \quad (7)$$

Here each of the expansion coefficients, K's, is constant for a fixed $\tilde{\nu}$-value:

$$K_i(\tilde{\nu}) = \sum_{m=0}^{i} \frac{n!(-1)^{i-m}}{(n-i)!(i-m)!} f^\circ_{mR}(\tilde{\nu}) \quad (8)$$

with the boundary conditions,

$$K_0(\tilde{\nu}) = f(\tilde{\nu}, 0) = f^\circ_A(\tilde{\nu}) \quad (9)$$

and

$$\sum_n K_n(\tilde{\nu}) = f(\tilde{\nu}, 1) = f^\circ_B(\tilde{\nu}). \quad (10)$$

Case of n=2. For a special case n=2 in Eq. 7, the following coefficients are obtained from Eq. 8:

$$K_2(\tilde{\nu}) = f^\circ_{0R}(\tilde{\nu}) + f^\circ_{2R}(\tilde{\nu}) - f^\circ_{1R}(\tilde{\nu}), \quad (11)$$

$$K_1(\tilde{\nu}) = 2\{f^\circ_{1R}(\tilde{\nu}) - f^\circ_{0R}(\tilde{\nu})\}, \quad (12)$$

and

$$K_0(\tilde{\nu}) = f^\circ_{0R}(\tilde{\nu}). \quad (13)$$

Discussion

If a PBQ molecule is located substitutionally at any of centrosymmetric sites in the DCB or DBB lattice of monoclinic $P2_{1/a}$, the zero-phonon origin band in the $^3B_{1g}\rightarrow{}^1A_g$ phosphorescence of the PBQ molecule is forbidden by the electric dipole selection rule. The weak origin band observed in these hosts[2,3] seems to support the assumption mentioned above for the molecular location in the hosts. When a PBQ molecule is located at any of noncentrosymmetric sites in the BCB or toluquinone lattice, however, the intensification of the origin band is remarkable (see Fig. 2a and also Ref. 9).

The intensity change observed in the binary solvent system of DCB and DBB is extremely suggestive (*cf.* Figs. 3 and 4). Supposing that one of the host molecules is substituted with a guest PBQ molecule, we can, as the zeroth approximation, consider a model in which the PBQ molecule is surrounded by eighteen neighbor host molecules: Six of them are located at "translationally equivalent" sites and the others at "translationally nonequivalent" ones. In the present case any possible guest-guest interaction is neglected since the concentration of the guest employed is dilute enough. As has been demonstrated in the previous works on the Stark experiments,[5,6,16,28] the most effective electric perturbation for the interstate coupling between $^3B_{1g}(n\pi^*)$ and $^3A_u(n\pi^*)$ states is the electric field change along the C=O axis of the guest molecule. This will be true for environmental dipolar perturbations or asymmetric host locations. As a matter of fact, a preliminary model calculation shows that the effective electric field of a permanent host molecule with 10^{-1} D over a guest molecule distant by 8 Å from it amounts to $\approx 10^6$ V/cm in external bulk scales.[29]

It is thus expected that the host arrangements concerning with four translationally equivalent molecules along the crystallographic b and c axes (*e.g.*, the molecule I′ for the assumed guest molecule I in Fig. 1) give

little contribution to the interstate mixing between $^3B_{1g}$ and ^3A_u states as well as those concerning with six translationally nonequivalent molecules (*e.g.*, the molecule II'). Furthermore, two translationally equivalent molecules along the a-axis are located too far from the guest molecule to be taken into account. There remain six translationally nonequivalent molecules on which the effective C=O axis perturbations should be assessed (*e.g.*, see the molecules II at (a/2, b/2, −c), (a/2, b/2, 0), and (a/2, b/2, c); and their inversion sites with respect to the site I). However, several investigations on the phosphorescence spectra have suggested that the $\pi_5^* \leftarrow n_\pm$ excitations are localized on the C=O groups.[6,14] Since the closest halogen-halogen intermolecular distances of DCB and DBB have been reported to be 3.85 Å and 3.76 Å, respectively, between the molecule I at (0, 0, 0) and the molecule II at (a/2, b/2, 0),[17] it seems reasonable to consider the molecule II and its inversion site molecule $\overline{\text{II}}$ at (−a/2, −b/2, 0) as the most effective components of anisotropic force-fields. There are four ways in which the molecules of DBB(B) and DCB(C) occupy these sites:

$$\text{II(B)–}\overline{\text{II}}\text{(B)},\ \text{II(C)–}\overline{\text{II}}\text{(C)},\ \text{II(B)–}\overline{\text{II}}\text{(C)},$$
$$\text{and II(C)–}\overline{\text{II}}\text{(B)}.$$

If we define the emission shape functions for these host arrangements as $f_B(\tilde{\nu})$, $f_C(\tilde{\nu})$, $f_{BC}(\tilde{\nu})$, and $f_{CB}(\tilde{\nu})$, respectively, an actual emission shape $f(\tilde{\nu}, x)$ will be represented by means of the usual statistical treatment:

$$\begin{aligned} f(\tilde{\nu}, x) &= x_{DBB}^2 f_B(\tilde{\nu}) + x_{DCB}^2 f_C(\tilde{\nu}) \\ &\quad + x_{DBB}x_{DCB}\{f_{BC}(\tilde{\nu}) + f_{CB}(\tilde{\nu})\} \\ &= x^2 f_B(\tilde{\nu}) + (1-x)^2 f_C(\tilde{\nu}) + 2x(1-x) f_{BC}(\tilde{\nu}). \end{aligned} \quad (14)$$

This just corresponds to what is given for the special case of $n=2$ in the preceding section (*cf.* Eqs. 11—13). Certainly, intensity contributions from higher orders of x than x^2 are expected small for small values of x, but this good agreement between the observed intensity change and the simulation curve of $n=2$ around $x \approx 1$ strongly supports our assumption for effective host arrangements. Since each lattice point of the mixed crystal is regarded as a statistical average of the binary components of molecules,[20] the resemblance between the phosphorescence spectra of PBQ/BCB and PBQ/(0.5 molar fraction of DCB+0.5 molar fraction of DBB) seems to be reasonable. It is suggested that the asymmetric arrangement between the molecular location II in Fig. 1 and its inversion one $\overline{\text{II}}$ is very effective for increasing the "origin band" of the PBQ phosphorescence in intensity. Similar intensification of "forbidden" bands of molecules in environments have extensively been discussed and importance of the environmental effects has been emphasized.[30–33]

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