The Electronic Absorption and Emission Spectra of Biphenylene-2,3-dione in Solutions

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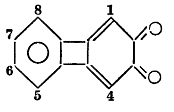
The electronic absorption and MCD spectra and phosphorescence spectra at 77 K, in solutions, have been studied by the use of P-P-P-method calculations. The longest-wavelength S–S $\pi\pi^*$ band, near 370 nm, is proved to consist of two $\pi\pi^*$ bands, the $^1A_1$ and $^1B_2$ bands. The $n\pi^*$ absorption, and phosphorescence bands in various kinds of solutions are compared in many respects with those of the *o*-quinones previously studied.

Previously, we have theoretically and experimentally studied the electronic absorption spectra of the *o*-quinones, *o*-benzoquinone,[1–3] and 1,2-naphthoquinone,[1,4,5] and the electronic absorption and emission spectra of the *o*-quinones, acenaphthenequinone,[4,6,7] and 9,10-phenanthrenequinone,[1,4,6,8,9] in solutions. Heretofore, however, the $n\pi^*$ absorption spectra of *o*-benzoquinones have not been studied in detail because of their instability. The emission spectra of *o*-benzoquinones and 1,2-naphthoquinones have never been reported, either, as far as we know. Biphenylene-2,3-dione[11,12] (BPD), which may be classified as a *o*-benzoquinone, is stable and is unique for its containing a fused four-membered ring. As for BPD, only the positions and intensities of its $\pi\pi^*$ absorption maxima in a solution have been reported. Therefore, we have studied the $\pi\pi^*$ and $n\pi^*$ absorption and emission spectra of BPD in solutions.



BPD

Experimental

Measurements. The absorption spectra in solutions were measured in the same manner as in previous works.[3–5,8] The magnetic circular dichroism (MCD) spectra in solutions were obtained by means of a J-20C recording spectropolarimeter of the Japan Spectroscopic Co., with a magnetic field of 0.93 T. The magnetic field was measured by means of a gauss meter. The phosphorescence spectra in solutions at 77 K were measured in the same manner as in previous works.[6,7,9] The dichroism of the phosphorescence spectrum in the 1-chlorobutane solution was measured by the photoselection method.[6,13]

Materials. BPD prepared by Sato *et al.*[12] was used (mp 213.5—214.5 °C).[14] Commercially available cyclohexane, methylcyclohexane, carbon disulfide, toluene, dioxane, methanol, 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) of a spectro-grade, and 1-chlorobutane of Tokyo Kasei's Special Use grade were used without further purification. Commercially available chloroform of a special grade was washed five times with water, dried with calcium chloride, and distilled.

Results. The absorption, MCD, and phosphorescence spectra obtained are shown in Figs. 1—4. The wavelengths and molar absorption coefficients of the absorption maxima, and the oscillator strengths of the absorption bands are shown in Table 1. The band names in Table 1 will be presented later. The MCD spectra in the toluene and cyclohexane solutions were similar to that in the 1-chlorobutane solution in Fig. 3. The MCD spectra were obtained with a relatively high noise-level because a low magnetic field was used. However, their accuracy is thought to be

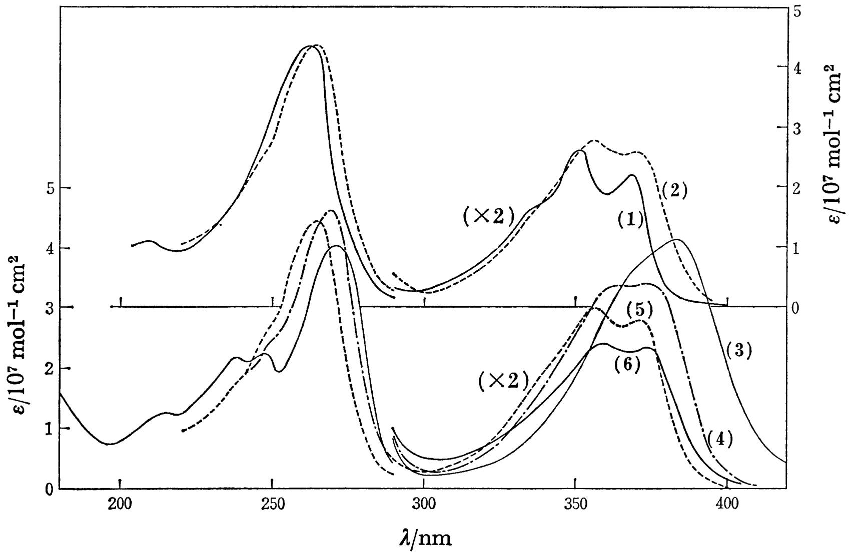


Fig. 1. Absorption spectra of biphenylene-2,3-dione in solutions.
Solvent: (1) methylcyclohexane, (2) dioxane, (3) 1,1,1,3,3,3-hexafluoro-2-propanol, (4) chloroform, (5) 1-chlorobutane, (6) toluene.
(In (1) the scale of the ordinate is arbitrary.)

not so low as to affect the discussion in this work. The wavelengths of the phosphorescence maxima were 575, 579, and 584 nm for the 1-chlorobutane, dioxane, and toluene solutions respectively. As for the dichroism of the phosphorescence-excitation spectrum, the qualitative results to be presented later were obtained. The lifetimes of the phosphorescence bands have not yet been accurately obtained with the phosphoroscope, partly because these phos-

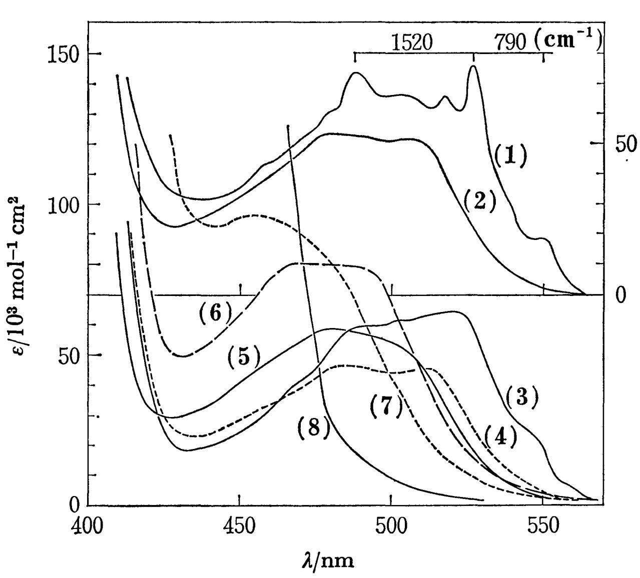


Fig. 2. Absorption spectra of biphenylene-2,3-dione in solutions.
Solvent: (1) methylcyclohexane, (2) 1-chlorobutane, (3) carbon disulfide, (4) toluene, (5) dioxane, (6) chloroform, (7) methanol, (8) 1,1,1,3,3,3,-hexafluoro-2-propanol.
(In (1) the scale of the ordinate is arbitrary.)

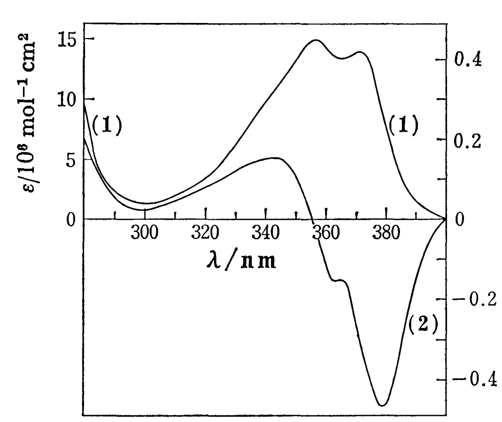


Fig. 3. Absorption and MCD spectra of biphenylene-2,3-dione in 1-chlorobutane.
(1) absorption spectrum, (2) MCD spectrum.

Table 1. Wavelengths, energies, and molar-absorption coefficients of the absorption maxima and oscillator strengths of the absorption bands

Solvent	$\frac{\lambda}{\text{nm}}$	$\frac{E}{\text{eV}}$	$\frac{\varepsilon}{10^3\ \text{mol}^{-1}\ \text{cm}^2}$	f	Band
Methylcyclohexane	550	2.25			nπ*
	527	2.35			
	517	2.40			
	488	2.54			
	369	3.36			a₁, a₂
	351	3.53			
	261	4.75			b
	210	5.90			d
1-Chlorobutane	505	2.45	51.5	0.00080	nπ*
	479	2.59	53.8		
	371	3.34	13850	0.242	a₁, a₂
	356	3.48	14850		
	265	4.68	44000	0.99	b
1,1,1,3,3,3-Hexafluoro-2-propanol	382.5	3.24	20600	0.34	a₁, a₂
	271	4.57	40500	0.63	b
	247.5	5.01	22350	0.48	c
	238	5.21	21700		
	213	5.82	11900	0.23	d
Chloroform	475		80.0	0.00120	nπ*
	374		16850		a₁, a₂
	362		16700		
	269.5		46100		b
Toluene	512.5		45.5	0.00068	nπ*
	481		46.0		
	372.5		11700		a₁, a₂
	359		11900		
Dioxane	479		58.5		nπ*
	370.5		12850		a₁, a₂
	355.5		13800		
	265		43550		b
Carbon disulfide	521		64.3	0.00092	nπ*
Methanol	456		96.2		nπ*

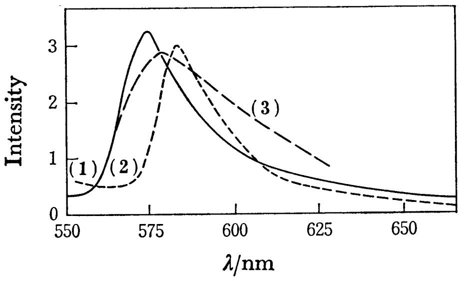


Fig. 4. Phosphorescence spectra of biphenylene-2,3-dione in solutions at 77 K.
Solvent: (1) 1-chlorobutane, (2) toluene, (3) dioxane.

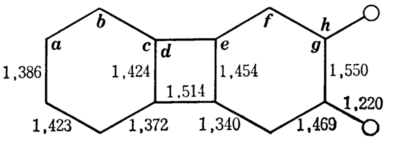


Fig. 5. Dimensions of biphenylene-2,3-dione.
a: 123°, b: 115°, c: 123°, d: 90°, e: 122.5°, f: 120°, g: 117.5°, h: 122°.

phorescence bands are weak and partly because their lifetimes are short. They were estimated to be around 0.3 ms on the basis of the observed relationships between the phosphorescence intensities and the rotational speeds of the phosphoroscope.

Calculations

Method. The electronic integral values for BPD in the P-P-P method[15] were the same as those previously used for other quinones,[3,5,8] except for those of the core-resonance integrals. Since BPD containes a fused four-membered ring, the core-resonance integrals between non-adjacent atoms were also included. The core-resonance integral (β_{ij}) between the i-th and j-th atoms was obtained according to the following formula;

$$\beta_{ij} = -31.35 \exp(-1.86 R_{ij}) \text{ (eV)},$$

except for those of the carbonyl bonds, which were taken as −2.5 eV, as in the previous works.[3,4,8] R_{ij} (Å) denotes the bond distance between the two atoms. This formula gives values close to those previously used for *o*- and *p*-benzoquinones and 9,10-anthraquinone,[3] −2.0, −2.5, and −2.3 eV for the conventional single and double bands and the benzene bonds respectively. The changes in the excitation energy of the lowest $\pi\pi^*$ states of BPD with the alkyl-group substitutions were also calculated in the same manner as in the previous works.[3,5,8] In the calculations, the thirty lowest singly excited configurations were included. The dimensions of BPD shown in Fig. 5, where the molecular structure of BPD is planar and has the C_{2v} symmetry,[16] were assumed considering the previously reported dimensions of *o*-benzoquinone[17] and biphenylene.[18]

Results. The calculated results for the lower singlet excited states are shown in Table 2. The molecular plane and symmetry axis of BPD are regarded as the yz-plane and the z-axis respectively. In this table, the first column denotes an order based on the magnitudes of the calculated excitation energies. Y and Z in the second column denote the directions of the elctronic-transition moments from the ground state. The assignment in the last column will be discussed later.

Table 2. The calculated results

No.	Symmetry	$\frac{E}{\text{eV}}$	f	Band
1	$^1B_2$(Y)	3.68	0.137	a_1
2	$^1A_1$(Z)	3.75	0.102	a_2
3	$^1B_2$	4.44	0.094	
4	$^1A_1$	4.51	0.003	
5	$^1A_1$	4.71	1.895	b
6	$^1B_2$	4.98	0.002	
7	$^1B_2$	5.37	0.206	c

Discussion

In Figs. 1 and 2, an $n\pi^*$ band is observed near 500 nm and four $\pi\pi^*$ bands appear to be near 370, 260, 240, and 210 nm, the 260 nm band being the strongest. These four $\pi\pi^*$ bands are denoted as the a-, b-, c-, and d-bands respectively. The largest red-shift of the a- and b-bands, and the large intensification of the a-band in the HFP solution in comparison with the cases of other solutions, are noticeable. Those facts may be attributed to the strong hydrogen-bond formation between BPD and HFP.[5,8] The fact that the intensity near 300 nm of the $\pi\pi^*$ absorption spectrum in the toluene solution is stronger than those in other solutions shows that, in this wavelength region, there is an intermolecular charge-transfer band between toluene and BPD. The emission bands in Fig. 4 may be assigned to the $n\pi^*$ phosphorescence band in view of their positions relative to those of the $n\pi^*$ absorption bands in Fig. 2 and their short lifetimes. Previously, similar $n\pi^*$ phosphorescence bands have been observed for 9,10-phenanthrenequinone[9] and acenaphthenequinone,[7] as will be discussed later. Therefore, the lowest triplet state of BPD may be the $n\pi^*$ state, as in the case of the other *o*-quinones.[6,7,9]

The MCD spectrum in Fig. 3, clearly shows that the a-band consists of two $\pi\pi^*$ bands, where the MCD signs of the longer and shorter wavelength bands are minus and plus respectively.[19,20] The observed dichroism of the phosphorescence-excitation spectrum is consistent with this fact and shows that the above-mentioned shorter wavelength band has its absorption maximum, which may be its 0-0 band, near the second peak of the a-band. These two $\pi\pi^*$ bands are denoted as the a_1- and a_2-bands for the longer and shorter wavelength bands respectively. Furthermore, the dichroism of the phosphorescence-excitation spectrum shows that the direction of the polarization of the a_1- and c-bands and that of the a_2- and b-bands are the same as, and different from, that of the phosphorescence band respectively.

The assignments of the a_1-, a_2-, b-, and c-bands are shown in the last column in Table 2. As may be seen from the comparison between the observed

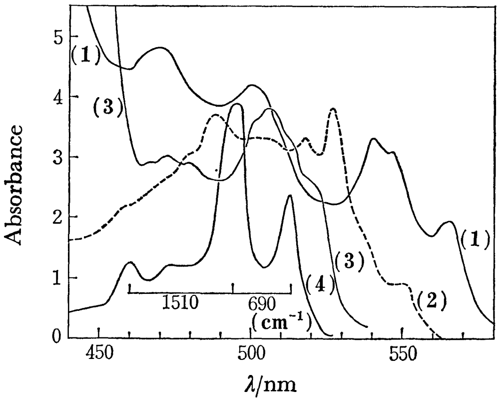


Fig. 6. nπ* Absorption bands of *o*-quinones in heptane solutions.

(1) 1,2-naphthoquinone, (2) biphenylene-2,3-dione, (3) 9,10-phenanthrenequinone, (4) acenaphthenequinone.

(In biphenylene-2,3-dione the solvent is methylcyclohexane.)

and calculated results, these assignments seems reasonable. Therefore, the a_1- and c-bands and the phosphorescence band may be said to be polarized along the short axis (Y-axis) of BPD, and the a_2- and b-bands to be polarized along the long axis (Z-axis). The assignment of the d-band is ambiguous. The calculated results show that the excited state of the a_1-band is of the local excitation type in the benzoquinone group and is similar to that of the longest-wavelength ππ* ($^1B_2$) band (near 370 nm) of *o*-benzoquinone.[3] However, the intensity of the a_1-band is far larger than that of the corresponding band of *o*-benzoquinone.[1,10] As for the changes in the calculated excitation energy of the lowest ππ* states (the Nos. 1 and 2 states) of BPD with the symmetrical two-alkyl-group substitutions, a relatively large energy decrease in the No. 1 state of 1,4-dialkyl-BPD was found.

Since it is generally accepted, on the basis of the observed photoelectron spectra, that the energy difference between the n_+ and n_- orbitals[21] of α-dicarbonyls is *ca.* 2 eV,[22,23] where the n_+ orbital energy is higher, the nπ* bands of BPD in Fig. 2 may contain only the $\pi^* \leftarrow n_+$ transition band,[24] as in the case of the α-diketones.[23,25] The nπ* absorption bands of the *o*-quinones in saturated hydrocarbon solutions are situated in the following order from the longer wavelength side, as may be seen from a comparison of Figs. 2 and 6:

o-Benzoquinone > 1,2-Naphthoquinone > BPD

> 9,10-Phenanthrenequinone > Acenaphthenequinone.

The nπ* band of *o*-benzoquinone[1,10] is situated at far longer wavelengths than those of the other *o*-quinones.[4] This order is just the reverse of that in the numbers of carbon atoms in the π-electronic systems of these *o*-quinones, except for the case of acenaphthenequinone. A similar phenomenon is observed in the *p*-quinones[4,26] (*p*-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone).

As for the nπ* bands of BPD in Fig. 2, it is noticeable that its blue-shift in the dioxane solution, in comparison with the case of the saturated hydrocarbon solutions, is smaller than those in other *o*-quinones,[4] acenaphthenequinone, 9,10-phenanthrenequinone, and 1,2-naphthoquinone, which are remarkably large, and that its intensity remarkably increases with the hydrogen-bond formation between BPD and the protic solvents, as may be seen from a comparison between the cases of toluene and the protic solvents, chloroform, and methanol. The former point corresponds to a fact about the phosphorescence bands which will be presented later. This point may show that the charge-transfer interaction between dioxane and BPD is weaker than those between dioxane and other quinones. The calculated π-electronic structures of these *o*-quinones give no information about this difference between BPD and other *o*-quinones. As for the latter point, nothing similar is observed in acenaphthenequinone,[4] but in the thiocarbonyl nπ* band of styrene trithiocarbonate[27,28] there is a similarity. This intensity enhancement may be due to the symmetry degradation of the n_+ orbital of BPD and the increased mixing of the nπ* and its neighbouring ππ* states, accompanied by the decreased energy gap between them, resulting from the hydrogen-bond formation. Acenaphthenequinone's failure to show anything similar may be an interesting problem to be solved in future.

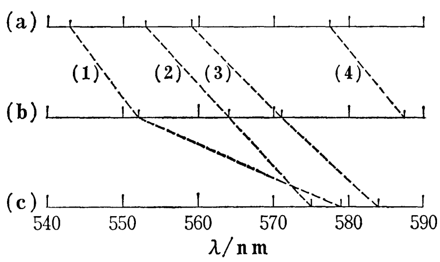


Fig. 7. Positions of nπ* phosphorescence bands of *o*-quinones in solutions.

(a) Acenaphthenequinone, (b) 9,10-Phenanthrenequinone, (3) Biphenylene-2,3-dione.

(1) Dioxane, (2) 1-chlorobutane, (3) toluene, (4) heptane.

In the nπ* band in the methylcyclohexane solution, the energy difference between the longest-wavelength shoulder near 550 nm and the sharp peak at 527 nm is *ca.* 790 cm⁻¹, while the one between the two main peaks at 527 and 488 nm is *ca.* 1520 cm⁻¹, as is shown in Fig. 2. A similar vibrational structure is also observed in the case of acenaphthenequinone, though the intensity distributions are different, as may be seen in Fig. 6. The structures of 790 cm⁻¹ and 1520 cm⁻¹ may be assigned to the ring-breathing[29] and C–O stretching vibrations respectively.

In the nπ* phosphorescence bands in Fig. 4, only the 0-0 band appears clearly; this pattern is similar to those in 9,10-phenanthrenequinone[9] and acenaphthenequinone.[7] No phosphorescence band can be observed in saturated hydrocarbon solutions. The estimated lifetimes (*ca.* 0.3 ms) are far shorter than those in the above two *o*-quinones, which are around 10 ms.[6,7,9] A similar difference is observed between *p*-benzoquinone (*ca.* 0.08 ms)[30,31] and 9,10-anthraquinone (*ca.* 3 ms).[6,32] The phosphorescence band in the dioxane solution is situated between those in the 1-chlorobutane and toluene solutions, while in the above two *o*-quinones[7,9] it is at far shorter wavelengths than the others, as may be seen in Fig. 7. This fact is consistent with the before-mentioned fact about the nπ^* absorption band of BPD in the dioxane solution.

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References

1) S. Nagakura and A. Kuboyama, *Nippon Kagaku Zasshi*, **74**, 499 (1953); *J. Am. Chem. Soc.*, **76**, 1003 (1954); A. Kuboyama, *Bull. Chem. Soc. Jpn.*, **32**, 1226 (1959).

2) A. Kuboyama and K. Wada, *Bull. Chem. Soc. Jpn.*, **38**, 1709, (1965); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **63**, 123 (1968).

3) A. Kuboyama, S. Matsuzaki, M. Takagi, and H. Arano, *Bull. Chem. Soc. Jpn.*, **47**, 1604 (1974); *J. Nat. Chem. Lab. Ind.*, **69**, 492 (1974).

4) A. Kuboyama, *Bull. Chem. Soc. Jpn.*, **33**, 1027 (1960); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **57**, 541 (1962).

5) A. Kuboyama and H. Arano, *Bull. Chem. Soc. Jpn.*, **49**, 1401 (1976); *J. Nat. Chem. Lab. Ind.*, **72**, 170 (1977); A. Kuboyama and H. Matsumoto, *Bull. Chem. Soc. Jpn.*, **52**, 1796 (1979).

6) A. Kuboyama and S. Yabe, *Bull. Chem. Soc. Jpn.*, **40**, 2475 (1967); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **64**, 105 (1969).

7) A. Kuboyama and S. Matsuzaki, *Nippon Kagaku Kaishi*, **1973**, 2248; *J. Nat. Chem. Lab. Ind.*, **69**, 69 (1974).

8) A. Kuboyama, F. Kobayashi, and S. Morokuma, *Bull. Chem. Soc. Jpn.*, **48**, 2145 (1975); *J. Nat. Chem. Lab. Ind.*, **71**, 180 (1976); A. Kuboyama, *Chem. Phys. Lett.*, **41**, 544 (1976); *J. Nat. Chem. Lab. Ind.*, **73**, 348 (1978).

9) A. Kuboyama and M. Anze, *Nippon Kagaku Kaishi*, **1972**, 229; *J. Nat. Chem. Lab. Ind.*, **67**, 165 (1972).

10) S. Goldschmidt and F. Graef, *Chem. Ber.*, **61**, 1858 (1928); H. J. Teuber and G. Staiger, *ibid.*, **88**, 802 (1955); DMS, "UV Atlas of Organic Compounds," Butterwoths (1968), B8/27.

11) J. M. Blatchly, J. F. W. McOmie, and S. D. Thatte, *J. Chem. Soc.*, **1962**, 5090.

12) M. Sato, H. Fujino, S. Ebine, and J. Tsunetsugu, *Bull. Chem. Soc. Jpn.*, **50**, 3076 (1977).

13) J. R. Lombardi, J. W. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964); J. Czekalla, W. Liptay, and E. Döllefeld, *Ber. Bunsenges. Phys. Chem.*, **68**, 80 (1964).

14) The BPD was furnished by the courtesy of Prof. S. Ebine of the Faculty of Science of Saitama University.

15) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

16) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, New York (1944), p. 384.

17) A. L. Macdonald and J. Trotter, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 476.

18) T. K. Fawcett and J. Trotter, *Acta Cristallogr.*, **20**, 87 (1966); T. C. W. Mak, *J. Chem. Soc.*, **1962**, 1.

19) Since BPD has no degenerate state, its MCD spectrum is of the B type (A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966)).

20) A. Kuboyama, *Bull. Chem. Soc. Jpn.*, **52**, 329 (1979); *J. Nat. Chem. Lab. Ind.*, **75**, 315 (1980).

21) n_+ and n_- orbitals denote the bonding (+) and antibonding (−) combinations of the two high-energy nonbonding orbitals of the two oxygen atoms of BPD.

22) D. Dougherty, P. Brint, and S. P. McGlynn, *J. Am. Chem. Soc.*, **100**, 5597 (1978).

23) J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970).

24) Since the calculated energy of the lowest $\pi^*(b_1)$ orbital is lower by 0.86 eV than that of the second lowest $\pi^*(b_2)$ orbital, the nπ^* band may be the out-of-plane polarized $^1B_1$ band. Accordingly, the nπ^* phosphorescence band may also be the $^3B_1$ band.

25) J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, *J. Am. Chem. Soc.*, **96**, 4386 (1974).

26) DMS, "UV Atlas of Organic Compounds," Butterworths (1968), B8/10.

27) Y. Jinnouchi, N. Kōno, and A. Kuboyama, The Abstracts of the 36th National Meeting of the Chemical Society of Japan (1977), p. 403.

28) In the nπ^* bands of 9,10-phenanthrenequinone and 1,2-naphthoquinone, the effect of the hydrogen-bond formation is difficult to examine because of the proximity of the nπ^* band and its neighbouring $\pi\pi^*$ band.

29) S. N. Singh and R. S. Singh, *Current Sci.*, **36**, 624 (1967); S. N. Singh, M. G. Jayswal, and R. S. Singh, *Bull. Chem. Soc. Jpn.*, **42**, 2048 (1969).

30) A. Kuboyama and S. Matsuzaki, The Abstracts of the 26th Annual Meeting of the Chemical Society of Japan (1972), p. 277.

31) G. Briegleb, W. Herre, and D. Wolf, *Spectrochim. Acta*, **25A**, 39 (1969).

32) A. Kuboyama, *Bull. Chem. Soc. Jpn.*, **43**, 3373 (1970); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **66**, 176 (1971).