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Studies of the $\pi\rightarrow\pi^*$ Absorption Bands of 9,10-Phenanthrenequinone

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The $\pi\rightarrow\pi^*$ S–S absorption spectra of 9,10-phenanthrenequinone and 3-bromophenanthrenequinone in solutions up to the vacuum UV region were obtained. On the other hand, MO calculations of the π-electronic systems of these quinones were carried out by means of the P–P–P method. The $\pi\rightarrow\pi^*$ absorption bands of these quinones were assigned on the basis of the calculated results. The blue-shift of the longest-wavelength $\pi\rightarrow\pi^*$ band of phenanthrenequinone due to the bromine-atom substitution at its 3-position was observed. Similar facts are found in aromatic carbonyl compounds, fluorenone and acetophenone.

Previously, we have theoretically and experimentally studied the $\pi\rightarrow\pi^*$ singlet-singlet absorption bands of *p*-quinones (*p*-benzoquinone, α-naphthoquinone, and anthraquinone) and *o*-benzoquinone.[1)] The $\pi\rightarrow\pi^*$ absorption bands of 9, 10-phenanthrenequinone(PHQ) have been studied by few workers. We have obtained the electronic spectra of PHQ and 3-bromo-PHQ in solutions up to the vacuum UV (VUV) region, and carried out MO calculations of their π-electronic systems by means of the P-P-P method. Their $\pi\rightarrow\pi^*$ singlet-singlet bands have been assigned on the basis of the calculated results.

Experimental

Measurements. The absorption spectra were measured in the same manner as in the previous work.[1)] *n*-Heptane, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and ethanol were used as solvents. The measurement of the absorption spectrum of PHQ in the gas phase was also carefully carried out at *ca.* 200 °C with a 5-cm-path cell wrapped with a ribbon heater, using a Cary 14M recording spectrophotometer.

Materials. Commercially-available PHQ was purified by vacuum sublimation (mp 209.5—210.5 °C). The 3-bromo-PHQ was prepared according to Schmidt *et al.*'s method[2)] and recrystallized five times from acetic acid (mp 272.5—273.5 °C). The *n*-heptane was the same as that used in the previous work, while the ethanol was of the spectrograde from the Dozin Yakugaku Co. The HFIP of the Eastman Co. was used without further purification.

Results. The $\pi\rightarrow\pi^*$ absorption spectra obtained are shown in Figs. 1—3. The wavelengths and molar absorption coefficients of the absorption maxima in these spectra are shown in Table 1. The solubility of these quinones in *n*-heptane was too poor for us to determine their concentration. Especially, the absorption spectrum of 3-bromo-PHQ in the *n*-heptane solution in the VUV region could not be accurately measured because of its very poor solubility. The longer-wavelength $\pi\rightarrow\pi^*$ bands of PHQ in the gas phase could not be accurately measured because of their weak intensities.

Calculations

Method. As for the electronic integral values in the P-P-P method, various kinds of integral values were tentatively used, based on the results obtained in the previous calculations. The set of electronic integral values which brought about the best agreement between the calculated and the experimental results will now be described. The values of the one-center core integrals, the two-center core integral of the C–O bonds, and electron repulsion integrals are the same as those used in the previous calculations.[1)] The two-center core integral values of the C–C bonds were obtained with the Pariser-Parr method.[3)] In this calculation, the bromine atom substituted for PHQ is considered to participate in the π-electronic system of PHQ with a 3p lone electron-pair. The one-center

TABLE 1. WAVELENGTHS AND MOLAR ABSORPTION COEFFICIENTS OF THE ABSORPTION MAXIMA (THE VALUES IN PARENTHESES ARE THE LATTER)

PHQ				3-Bromo-PHQ		Band name
Gas	*n*-Heptane	Alcohol	HFIP	*n*-Heptane	HFIP	
~372 (nm)	398	414.5 (1480)	442 (1370)	390	~435 (1260)	a
	~332			~340		b′
~298	314	321 (4290)	333.5 (6080)	317.5	331 (9030)	b
			~275 (13500)	279.5	284 (14200)	c′
249	263 256	264.5 (31500) 256 (29400)	261 (31500) 253.5 (31500)	261.5	262.5 (32000)	c
				~220		d′
200.5	209.5	210 (31400)	210 (37000)	~200	205 (27700)	d
	178		182 (31600)	~178	182 (27500)	e

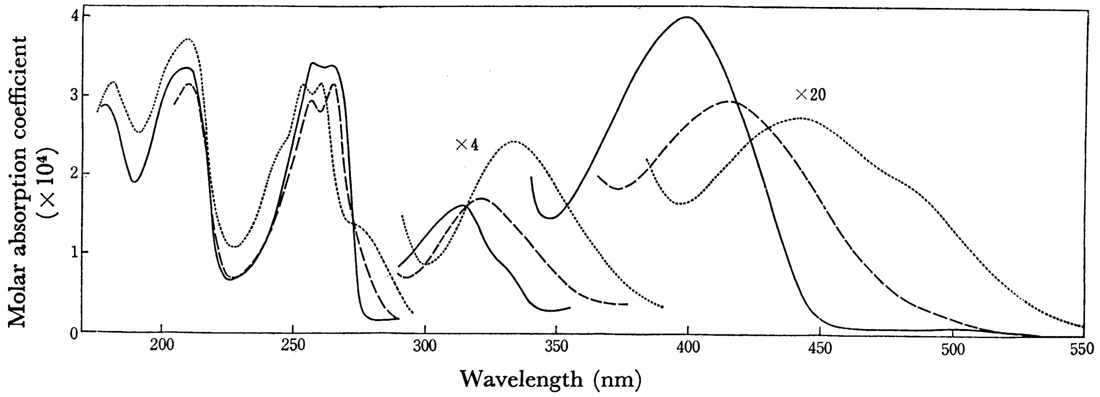

Fig. 1. Absorption spectra of phenanthrenequinone in solutions.
——: *n*-Heptane, — —: ethanol, ----: HFIP
In the *n*-heptane solution the scale of the ordinate is arbitrary.

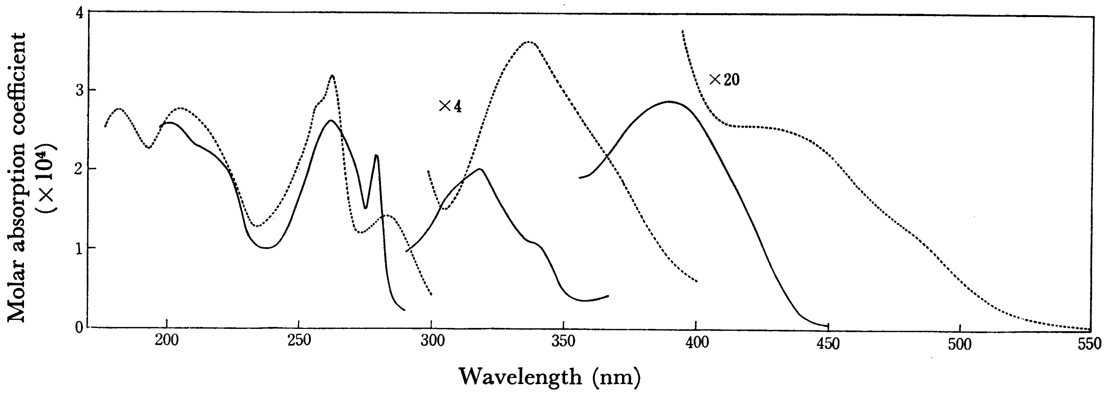

Fig. 2. Absorption spectra of 3-bromophenanthrenequinone in solutions.
——: *n*-Heptane, ----: HFIP.
In the *n*-heptane solution the scale of the ordinate is arbitrary.

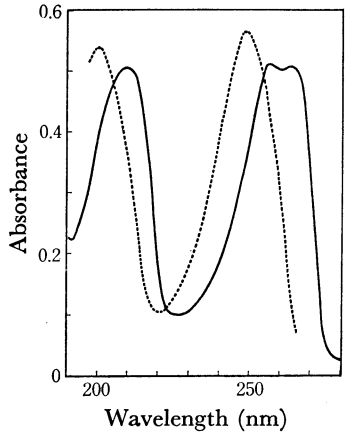

Fig. 3. Absorption spectra of phenanthrenequinone.
——: *n*-Heptane, ----: gas phase.
The scale of the ordinate is arbitrary.

core integral value of the bromine atom (−20.00 eV) and the two-center core integral value of the carbon-bromine bond (−1.00 eV) were determined so that the results calculated with them might be reasonable.

In the calculation, the forty lowest singly-excited configurations were included. The calculations were carried out with a FACOM 270-30 computer. The dimensions of PHQ assumed are shown in Fig. 4. The molecular structure of PHQ has not yet been elucidated.[4] PHQ is considered to take the planar structure of C_{2v} The dimensions shown in Fig. 4 were assumed considering the reported dimensions of its related compounds[5] (fluorene, triphenylene, anthraquinone, and acenaphthenequinone). The lengths of all the bonds in the benzene rings in PHQ were assumed to be 1.40 Å. The bond length of the carbon-bromine bond in 3-bromo-PHQ was assumed to be 1.91 Å.[6]

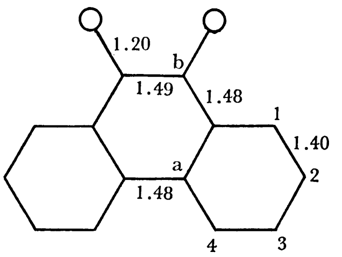

Fig. 4. Dimension of phenanthrenequinone (Å).
a: 120 °, b: 121.5 °.

Results. The calculated excitation energies (E), oscillator strengths (f), and symmetry species of the excited singlet states are shown in Table 2, along with the observed results in *n*-heptane solutions (for energies) and HFIP solutions (for f-values). The molecular plane and symmetry axis of PHQ are regarded as the yz-plane and the z-axis respectively.[7] The first column

Table 2. The calculated excitation energies, oscillator strengths, and symmetry species of the singlet excited states and the corresponding observed results

Calculated				Observed		
No.	Symmetry	E (eV)	f	Band name	E (eV)	f
		(1) PHQ				
1	$B_2(y)$	4.220	0.130	a	3.1	0.03
2	$A_1(z)$	4.302	0.001	b′	3.7	0.13
3	B_2	4.458	0.104	b	3.9	
4	B_2	5.138	0.504	c	4.8	0.78
5	A_1	5.155	0.461	c′		
9	B_2	5.925	0.625	d	5.9	1.0
10	A_1	6.046	0.641	d′		
18	B_2	6.638	0.297	e	7.0	∼0.7
20	A_1	6.871	0.204			
21	A_1	6.932	0.274			
22	A_1	7.178	0.618			
23	B_2	7.207	0.596			
		(2) 3-Bromo-PHQ				
1		4.215	0.109	a	3.2	∼0.02
2		4.272	0.014	b′	3.7	0.15
3		4.422	0.091	b	3.9	
4		5.057	0.548	c′	4.4	∼0.2
5		5.162	0.486	c	4.7	∼0.5
9		5.899	0.513	d′	5.6	0.9
10		5.972	0.423	d	6.2	
18		6.718	0.194	e	7.0	∼0.8
19		6.763	0.353			
22		7.009	0.445			
23		7.218	0.304			
24		7.316	0.315			

of this table indicates the numbering of the magnitude of E. The letters, y and z, in parentheses denote the direction of polarization in the electronic transition. In this table, the data on the higher excited states with small f-values have been omitted.

Discussion

As may be seen in Fig. 1, PHQ in the n-heptane solution appears to have five distinct $\pi\to\pi^*$ bands–near 400, 315, 260, 210, and 180 nm. These five $\pi\to\pi^*$ bands are denoted as, respectively, the a-, b-, c-, d-, and e-bands. As for the very weak shoulder near 490 nm of the a-band in the HFIP solution, it may be assigned to the $\mathrm{n}\to\pi^*$ band, since the $\mathrm{n}\to\pi^*$ band is observed near 500 nm in the n-heptane solution.[8] The $\mathrm{n}\to\pi^*$ band in the HFIP solution seems to be somewhat intensified, compared with that in the n-heptane solution, through a vibronic coupling of the two closely-situated excited states of the $\mathrm{n}\to\pi^*$ band and the a-band. In the b- and c-bands, a shoulder is clearly found on the longer-wavelength side of the b-band in the n-heptane solution and of the c-band in the HFIP solution. These weak shoulders show that another $\pi\to\pi^*$ band may exist there. In the case of 3-bromo-PHQ, as may be seen in Fig. 2, a distinct shoulder is found on the longer-wavelength side of the b- and d-bands, and a new absorption peak is found on the longer-wavelength side of the c-band. These shoulders and peak on the longer-wavelength side of the b- and c-bands may correspond respectively to the above-mentioned shoulders of PHQ. As for the shoulder on the longer-wavelength side of the d-band, another $\pi\to\pi^*$ band may exist there. The corresponding band of PHQ may be hidden in its d-band. Therefore, eight $\pi\to\pi^*$ bands are noticeable in 3-bromo-PHQ, and PHQ may be supposed to have the corresponding eight $\pi\to\pi^*$ bands. These other $\pi\to\pi^*$ bands are denoted as b′-, c′-, and d′-bands respectively, as is shown in Table 1. The large energy changes of the $\pi\to\pi^*$ bands in HFIP solutions compared with those in n-heptane solution, as may be seen in Figs. 1 and 2, may be mainly due to a strong hydrogen-bond formation between the quinones and HFIP, because HFIP, containing six electronegative fluorine atoms in its molecule, is thought to be a strong proton-donor.

Since longer-wavelength $\pi\to\pi^*$ bands usually show a red-shift due to the substitution of such an electron-donating group as a bromine atom to a π-electronic system, it is noticeable that the a-band of PHQ shifts towards shorter wavelengths due to the bromine-atom substitution at its 3-position, as may be seen in Figs. 1 and 2. Similar facts are found in the longest-wavelength weak $\pi\to\pi^*$ band near 380 nm of fluorenone[9] and that near 280 nm of acetophenone,[10] using 3-bromo, 3-methyl, and 3-methoxyfluorenones[11] and p-methyl and p-chloroacetophenones respectively. In all these cases, the electron-donating groups are substituted at the para-position of benzene rings to carbonyl groups. Therefore, similar facts may be expected to be generally observed in other aromatic carbonyl compounds.

As for the assignments of the $\pi\to\pi^*$ bands of PHQ and 3-bromo-PHQ, the five bands, a-, b-, b′-, c-, and c′-bands, can be reasonably assigned on the basis of the calculated results, as may be seen in Table 2. The c′-band can be reasonably assigned on the basis of the relatively large decrease in its excitation energy with the bromine-atom substitution. As for the higher-energy bands, the d-, d′-, and e-bands, the assignments based on the calculated results are not clear.

As for the above-mentioned blue-shift of the a-band upon the bromine-atom substitution, the calculated energy changes of the a-band with the bromine-atom substitutions at the various positions are shown in Table 3. In addition, those with the alkyl-group

Table 3. The changes of the calculated excitation energies of the a-band of PHQ with the bromine-atom and the alkyl-group substitutions at its various positions

Position	ΔE (eV)[a]	
	Bromine atom	Alkyl group
1	−0.042	−0.006
2	−0.046	−0.035
3	−0.005	+0.011
4	−0.072	−0.033

a) ΔE denotes the remainders where the excitation energies of PHQ are subtracted from the corresponding ones of 3-bromo-PHQ.

substitutions are also shown in Table 3. The calculations of the alkyl-group substituted PHQ's were carried out taking the one-center core-integral value of the substituted carbon atoms as −9.00 eV, in consideration of the inductive effect of the alkyl group, but disregarding its resonance effect, as in the previous work.¹⁾ As may be seen in Table 3, the calculated energy decrease of the a-band in 3-bromo-PHQ is far smaller than those in the other bromo-PHQ's. Therefore, the calculated results are not inconsistent with the observed results. On the basis of the calculated results shown in Table 3, a blue-shift of the a-band of 3-alkyl-PHQ compared with that of PHQ can also be expected.

As for the comparison of our theoretical assignment of the $\pi\rightarrow\pi^*$ bands of PHQ with the experimental facts[12–14)] previously reported, our assignment of the a-, c-, and c′-bands is consistent with the dichroic absorption spectra of PHQ in the stretched PVA sheet, reported by Inoue *et al.*[12)] but that of the b-band is inconsistent. The pattern of the calculated energies and *f*-values of the π, π^* excited states of PHQ are far more sensitive to the electronic integral values used than those in the quinones previously studied.[1)] Therefore, further studies of the assignment of the $\pi\rightarrow\pi^*$ bands of PHQ are desirable.

As may be seen in Fig. 3, the shapes of the $\pi\rightarrow\pi^*$ bands of PHQ in the gas phase are similar to those in the *n*-heptane solution.[15)] The broad shape of the $\pi\rightarrow\pi^*$ bands in the gas phase may be due to the measurement at a high temperature. It is noticeable that all the energies of the $\pi\rightarrow\pi^*$ bands in the gas phase are considerably larger than those in the *n*-heptane solution as may be seen in Table 1. The energy differences (in wave number) between the former and the latter are *ca.* 1760, *ca.* 1710, 1630, and 2140 cm^{-1} for the a-, b-, c-, and d-bands respectively. A similar fact is observed in anthraquinone.[16)]

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