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Studies of the π-π^* Absorption Bands of *p*-Quinones and *o*-Benzoquinone

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The π—π^* absorption spectra of *p*-benzoquinone, α-naphthoquinone, anthraquinone, and their derivatives, mainly in *n*-heptane up to the vacuum UV region, were obtained. On the other hand, MO calculations of the π-electronic systems of these *p*-quinones and *o*-benzoquinone were carried out by means of the P-P-P method. The π—π^* absorption bands of these quinones could be favorably assigned on the basis of the calculated results.

As for the assignments of the $\pi \rightarrow \pi^*$ absorption bands of quinones in the ultraviolet (UV) region, many theoretical works[1–3] have been carried out. However, it is very desirable to clarify the absorption spectra in the vacuum ultraviolet (VUV) region in assigning the $\pi \rightarrow \pi^*$ absorption bands. The VUV absorption spectra of quinones have never been reported. In this work, the $\pi \rightarrow \pi^*$ absorption spectra of *p*-benzoquinone (*p*-BQ), α-naphthoquinone (α-NQ), anthraquinone(AQ), and their derivatives have been obtained up to the VUV region. On the other hand, MO calculations of the π-electronic systems of these *p*-quinones and *o*-benzoquinone have been carried out by means of the P–P–P method in order to determine the assignments of the $\pi \rightarrow \pi^*$ bands of these quinones.

Experimental

Measurements. The absorption spectra in the UV region were measured with a Cary 14 M recording spectrophotometer, and those in the VUV region, with a VUV-3 recording spectrophotometer of the Japan Spectroscopic Co., Ltd. The sample chamber and detector system of the latter apparatus have been modified as is shown in Fig. 1 after our previous work[4] on ketone vapors. Quartz cylindrical cells with 0.1, 0.5, and 1 mm paths were used; the design was similar to that used by Tsubomura *et al.*[5] *n*-Heptane and 1,1,1,3,3,3-hexafluoroisopropanol were used as solvents; they could be used up to 175 and 170 nm respectively with an 0.1 mm-path cell, but the former was mainly used. Daifloil (polymer of trifluorochloroethylene) was also used for *p*-benzoquinone in the UV region for the purpose of comparison.

Materials. *p*-BQ, 2,5-dimethyl-, and 2,5-dichloro-*p*-BQs, AQ, and 2-*t*-butyl-AQ (commercial products) were purified by sublimation. α-NQ (commercial products) was purified by vacuum sublimation at 30 °C. 2,5-Di-*t*-butyl-*p*-BQ (commercial products) was twice recrystallized from cyclo-

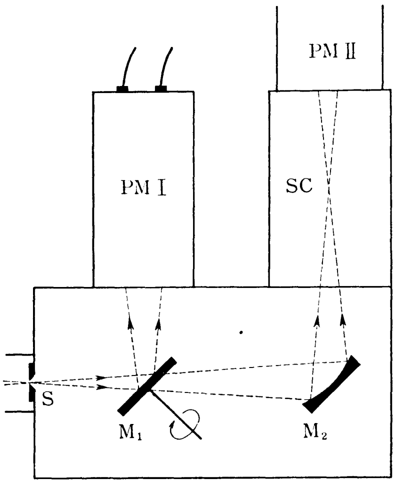

Fig. 1. The sample chamber and detector system
S: excit slit, M_1: plane rotating-sector mirror, M_2: concave mirror, SC: sample chamber, PMI and PMII: photomultiplyers (HTV R189).

Table 1. Wavelengths, energies and molar absorptivities of the absorption maxima

	λ_{max} (nm)	E_{max} (eV)	ε_{max}	Solvent
p-BQ	277	4.48	338	*n*-Heptane
	240.5	5.16	20000	
	295	4.20	310	1,1,1,3,3,3-hexafluoroisopropanol
	243	5.10	31000	
	171.5	7.23	15500	
	296	4.19	271	Daifloil
	243.5	5.09	27800	
2,5-Dimethyl-*p*-BQ	305	4.07	291	*n*-Heptane
	256.5	4.83	20500	
	248.5	4.99	23200	
	178	6.97	19000	
2,5-Di-*t*-butyl-*p*-BQ	305	4.07	294	*n*-Heptane
	261	4.75	15100	
	253	4.90	17800	
	175.5	7.07	23600	
2,5-Dichloro-*p*-BQ	325	3.82	340	*n*-Heptane
	270	4.59	26500	
	186.5	6.65	18700	
α-NQ	328	3.78	2840	*n*-Heptane
	245.5	5.05	21300	
	239.5	5.18	19100	
	193.5	6.41	38200	
2,3-Dimethyl-α-NQ	326	3.80	2510	*n*-Heptane
	268.5	4.62	18600	
	259.5	4.78	18100	
	247.5	5.01	18000	
	242	5.12	16200	
	192	6.46	41900	
AQ	332.5	3.73	3620	*n*-Heptane
	319.5	3.88	4800	
	270.5	4.58	18000	
	250.5	4.95	56800	
	204	6.08	36800	
	181	6.85	40400	
2-*t*-Butyl-AQ	321	3.86	5380	*n*-Heptane
	273.5	4.53	21000	
	255.5	4.85	54200	
	203	6.11	35800	
	182	6.81	37500	

hexane. 2,3-Dimethyl-α-NQ was prepared according to the methods described in the literature[6] and, was purified by vacuum sublimation. The melting points of all these purified samples agreed with those reported in the literature. *n*-Heptane was treated with conc. sulfuric acid and purified by silica gel chromatography. 1,1,1,3,3,3-Hexafluoroisopropanol (Eastman Co.) and Daifloil (#1; mean molecular weight, 500; Daikin Kogyo Co.) were used without further purification.

Results. The absorption spectra obtained are shown in Figs. 2—5. In Fig. 3, the absorption bands of 2,5-di-*t*-butyl- and 2,5-dichloro-*p*-BQs near 305 and 325 nm respectively are not shown; that of the former is very similar to that of 2,5-dimethyl-*p*-BQ. The wavelength (λ_{max}), energies (E_{max}), and molar absorptivities (ε_{max}) of the absorption maxima in these spectra are shown in Table 1. Since the solubility of AQ in *n*-heptane was too poor for us to determine its concentration, the molar absorptivities of the absorption maxima of AQ in *n*-heptane were obtained by assuming that of the band near 320 nm to be 4800, considering its value (4800) in cyclohexane, obtained by Brockmann.[7]

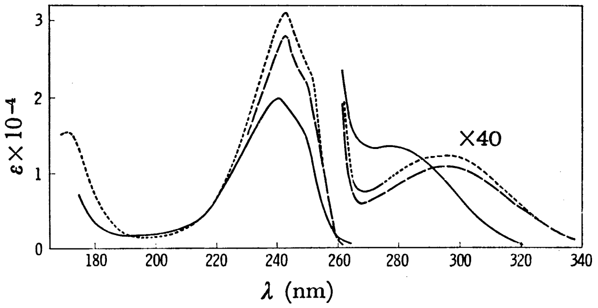

Fig. 2. Absorption spectra of *p*-benzoquinone in various solvents
——: *n*-heptane, ——: Daifloil, ----: 1,1,1,3,3,3-hexafluoroisopropanol

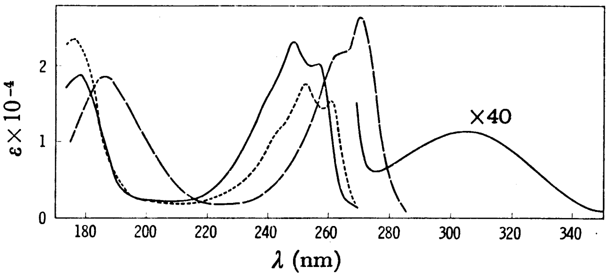

Fig. 3. Absorption spectra of *p*-benzoquinone substitutes in *n*-heptane
——: 2,5-dimethyl-, ----: 2,5-di-*t*-butyl-,
——: 2,5-dichloro-BQs

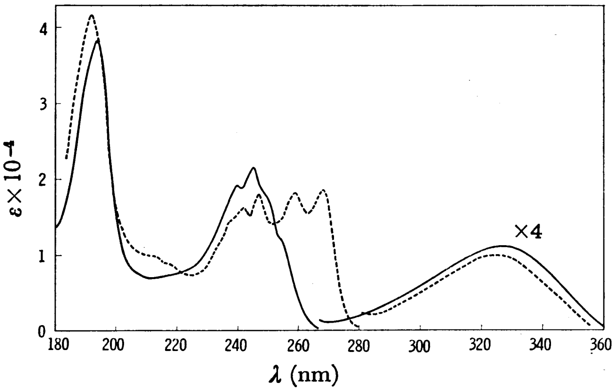

Fig. 4. Absorption spectra of α-naphthoquinones in *n*-heptane
——: α-naphthoquinone
----: 2,3-dimethyl-α-naphthoquinone

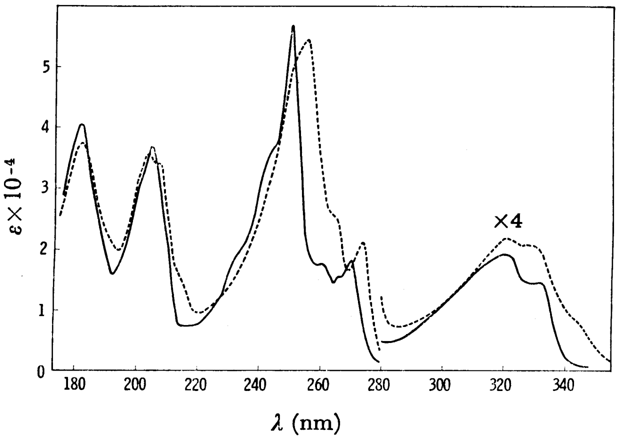

Fig. 5. Absorption spectra of anthraquinones in *n*-heptane
——: anthraquinone
----: 2-*t*-butyl-anthraquinone

Calculations

Method. As for the electronic integral values in the P-P-P method, various kinds of integral values were tentatively used, considering the results obtained in our previous calculation[1a] on the π-electronic system of *o*-BQ. Finally, it was proved that a good agreement between the calculated and the experimental results was generally obtained using the electronic integral values shown in Table 2. In this table, the suffix letters C and O denote the carbon and oxygen atoms respectively. U_C^* denotes the U_C of the carbonyl carbon atoms, while β_{CC}, β_{CC}^*, β_{CC}^{**}, and β_{CO} denote those of the conventional C–C single, double and benzene-ring bonds, and carbonyl C–O bond respectively. The values in brackets are those for α-NQ. The value of U_C is the same as that used in Hush and Pople's paper,[9] while that of $|U_O|$ seems to be too small in view of the valence-state ionization potential of the oxygen atom (17.25 eV).[10] As has been pointed out by Sidman,[2e] however, the U-term in Pople's SCF MO method[11] should be regarded as the valence-state orbital energy corrected for the fact that the atom is no longer isolated,

Table 2. Electronic integral values (eV)

(1) One-center core integrals	
U_C	−9.50
U_C^*	−10.00
U_O	−13.00
(2) Two-center core integrals	
β_{CC}	−2.00(−1.80)
β_{CC}^*	−2.50(−2.70)
β_{CC}^{**}	−2.30
β_{CO}	−2.50
(3) Electronic repulsion integrals	
Nishimoto-Mataga method[8]	

but is now a part of a molecule. From this point of view, the value of U_O may not be unreasonable. The value of U_C^* was taken in view of the π-electron densities being considerably smaller than those of other carbon atoms. In order to explain theoretically the effect of methyl-group substitution on the energy of the $\pi \rightarrow \pi^*$ bands of α-NQ, the calculation of 2,3-dimethyl-α-NQ was carried out taking the U_C value of the substituted carbon atoms as −9.00 eV, considering the inductive effect of the methyl group, but without considering its resonance effect. The values of β_{CC}, β_{CC}^*, and β_{CO}, except those for α-NQ, are the same as those of Case II in our previous work[1a)] on *o*-BQ and close to those used by Edwards *et al.*[3d)] in the calculations of conjugated carbonyl compounds. The values of β for carbon-carbon bonds are, except those for α-NQ, far less sensitive to the variation in C–C bond distance than those generally used.

In the calculations, all the singly-excited configurations were included except in the case of AQ, where the lowest forty configurations were included. The calculations were carried out with a FACOM 270-30 computer. The dimensions of the quinones assumed are shown in Fig. 6. Those of the three *p*-quinones were assumed according to the results of the X-ray analysis.[12–14)] The lengths of all the bonds in the benzene rings in α-NQ and AQ were assumed to be 1.40 A. The value for *o*-BQ was assumed on the basis of the bond orders obtained in our previous work.[1a)]

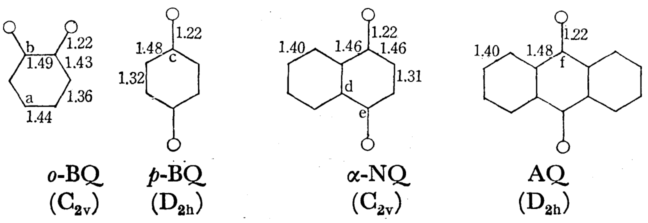

Fig. 6. Dimensions of the quinones (Å)
a: 120°, b: 121.5°, c: 117.5°, d: 118°, e: q118°, f: 117.5°

Results. The calculated excitation energies (E), oscillator strengths (f), and symmetry species[15)] of the excited singlet states are shown, along with the observed results in *n*-heptane solutions, in Table 3. In this paper, the molecular planes are regarded as yz-planes, and the symmetry axes of *o*-BQ and α-NQ and the C–O bond axes of *p*-BQ and AQ are regarded as z-axes. The first column of this table indicates the numbering of the magnitude of E. In this table, the data on the higher excited states with small f-values have been omitted.

Table 3. 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	E(eV)	f
		(1) *o*-BQ			
1	B_2	3.716	0.234	3.5	0.05
2	A_1	5.134	0.001		
3	B_2	5.442	0.146	4.9	~0.03
4	B_2	5.994	0.014		
5	A_1	6.310	1.106	~6.2	>0.2
7	A_1	7.421	0.405		
8	B_2	7.644	0.216		
10	B_2	7.946	0.320		
		(2) *p*-BQ			
1	B_{3g}	4.223	0	4.5	<0.01
2	B_{1u}	4.489	1.031	5.2	0.54
3	B_{3g}	5.471	0		
4	A_g	5.814	0		
5	B_{2u}	6.795	0.127		
7	B_{1u}	7.146	0.194		
8	B_{1u}	7.267	1.072	~7.2	~0.5
9	B_{2u}	8.070	0.233		
		(3) α-NQ			
1	A_1	4.213	0.028	3.8	0.08
2	B_2	4.468	0.178		
3	B_2	4.850	0.549	5.1	0.40
4	A_1	5.138	0.331		
5	B_2	5.629	0.018		
6	A_1	5.809	0.026		
9	A_1	6.366	0.617	5.6	0.1
12	B_2	7.126	1.251	6.4	0.68
14	A_1	7.293	0.301		
16	B_2	7.832	0.303		
		(4) AQ			
1	A_g	4.167	0		
2	B_{2u}	4.206	0.066	3.9	0.05
3	B_{3g}	4.418	0		
4	B_{1u}	4.564	0.647	4.6	0.15
5	A_g	5.135	0		
6	B_{2u}	5.180	0.888	5.0	0.61
7	B_{3g}	5.465	0		
8	B_{1u}	5.684	0.126		
12	B_{2u}	6.111	1.251	6.1	0.46
18	B_{1u}	6.913	1.619	6.9	0.80
30	B_{1u}	8.073	0.749		

Discussion

o- and p-*Benzoquinones.* The absorption spectra of *o*-BQ in solutions obtained by Goldschmidt *et al.*[16)] show that *o*-BQ has two $\pi \rightarrow \pi^*$ bands of a moderate intensity near 360 and 250 nm, and a strong $\pi \rightarrow \pi^*$ band near, 200 nm, or a little shorter than 200 nm.

The absorption spectra of *p*-BQ and its derivatives in Figs. 2 and 3 show that *p*-BQ has a weak $\pi \rightarrow \pi^*$ band[2f,17)] near 280 nm and two strong $\pi \rightarrow \pi^*$ bands near 240 and 170 nm. It is noticeable that the absorption intensity of the band near 240 nm of *p*-BQ in 1,1,1,3,3,3-hexafluoroisopropanol and Daifloil is considerably stronger than that in *n*-heptane, and that the relative intensity of the absorption maxima of the bands near 250 and 175 nm is considerably different between 2,5-dimethyl- and 2,5-di-*t*-butyl-*p*-BQs.

In *o*- and *p*-BQs, the correspondences between the calculated and observed results are excellent, and the excited states of the $\pi \rightarrow \pi^*$ bands mentioned above could be favorably assigned, as is shown in Table 3. The theoretical and experimentally-determined[2b,18)] assignments of the transitions of *p*-BQ in the UV region agree with each other. In our previous work[1a)] on *o*-BQ, the assignment of the band near 250 nm was uncertain, but it could be reasonably determined in

TABLE 4. THE CHANGES OF THE CALCULATED $\pi\to\pi^*$ EXCITATION ENERGIES OF α-NQ WITH THE SUBSTITUTION OF TWO METHYL GROUPS TO ITS 2- AND 3-POSITIONS

No.	ΔE (eV)	No.	ΔE (eV)
1	+0.016	6	−0.098
2	−0.023	9	−0.013
3	−0.200	12	−0.029
4	+0.046	14	+0.082
5	+0.005	16	+0.023

this work. In *o*-BQ, two or three $\pi\to\pi^*$ bands of a moderate intensity may be expected to be found in the VUV region, judging from the calculated results shown in Table 3.

α-Naphthoquinone. As may be seen in Fig. 4, α-NQ has three distinct $\pi\to\pi^*$ bands—that is, a relatively weak band near 330 nm and two strong bands near 245 and 195 nm. Besides these three bands, α-NQ appears to have a $\pi\to\pi^*$ band of a moderate intensity between the two bands near 245 and 195 nm. Furthermore, comparing the absorption spectrum of 2,3-dimethyl-α-NQ with that of α-NQ in Fig. 4, it is clear that the band near 245 nm of α-NQ is composed of two bands the intensities of which are of comparable order, and that one of these two bands remarkably shifts toward longer wavelengths with the substitution of two methyl groups at the 2- and 3-positions of α-NQ. The changes in the calculated $\pi\to\pi^*$ excitation energies of α-NQ with this substitution are shown in Table 4.[19] As may be seen in Table 4, only the No. 3 state shows a large energy decrease with this substitution. Therefore, the No. 3 state may be assigned to the excited state of the band which largely shifts toward longer wavelengths with that substitution. On the other hand, the band near 330 nm is quite broad; this band may be composed of two $\pi\to\pi^*$ bands. Considering the above discussion, the excited states of the $\pi\to\pi^*$ bands of α-NQ can be reasonably assigned as is shown in Table 3. The assignments of the bands in the UV region agree with those made by Titz *et al.*[3e]

Anthraquinone. As may be seen in Fig. 5, AQ has five distinct $\pi\to\pi^*$ bands—that is, a relatively weak band near 320 nm, and four strong bands near 270, 250, 205, and 180 nm. As may be seen in Table 3, the correspondences between the calculated and observed results for these five bands are excellent, and the excited states of these $\pi\to\pi^*$ bands can be favorably assigned.[20] The assignments of the bands in the UV region agree with those by Nishimoto *et al.*[3a] and Titz *et al.*[3e] and are consistent with the experimental facts obtained by many authors.[21] As for the No. 30 state in Table 3, a $\pi\to\pi^*$ band corresponding to this state is expected to be found at the wavelength region shorter than 170 nm.

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19) ΔE in Table 4 denotes the remainders where the $\pi\to\pi^*$ excitation energies of α-NQ are subtracted from the corresponding ones of 2,3-dimethyl-α-NQ.

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