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Studies of the $\pi\rightarrow\pi^*$ Absorption Bands of 1,2-Naphthoquinone

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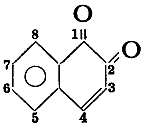
Synopsis. The $\pi\rightarrow\pi^*$ S–S absorption spectra up to the vacuum UV region of 1,2-naphthoquinone in solutions were obtained. Based on MO calculations, the observed five $\pi\rightarrow\pi^*$ bands of 1,2-naphthoquinone are assigned, and the alkyl-group substitution effects on the excitation energy of the longest-wavelength $\pi\rightarrow\pi^*$ band are discussed.

Previously, the present authors have theoretically and experimentally studied the $\pi\rightarrow\pi^*$ absorption bands of *p*-quinones[1] and 9,10-phenanthrenequinone[2] up to the vacuum UV region. In this note, the $\pi\rightarrow\pi^*$ absorption spectrum of 1,2-naphthoquinone (1,2-NQ), which has been studied by few workers, is reported.



The absorption spectra were obtained in the same manner as in that described in previous reports.[1,2] The solvents, heptane and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) were the same as those used in previous works.[1,2] The 1,2-NQ was prepared according to the Fieser method[3] (mp 146 °C with decomp.).

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

Heptane	HFP	Band name
382 (nm)	425 (2180)	I
338 326	354 (3370)	II
251 245	255 (27500) 249 (27500)	III
195	196 (24300)	IV
	~170 (~22500)	V

In the P-P-P method calculations, the electronic integral values used were the same as those used in previous calculations,[1,2] except for the core resonance integral values for the carbon–carbon bonds. The latter were taken to be −1.5, −2.7, and −2.3 eV for the conventional single and double bonds, and the benzene-ring bonds, respectively. These values are close to those obtained by the Pariser-Parr method,[4] except for that of the double bond which is smaller than the latter by *ca.* 0.2 eV. In the CI calculation, all the singly-excited configurations were included. The molecular structure of 1,2-NQ was assumed to be planar. The lengths of the C–O bonds, the C(1)–C(2) bond, conventional C–C single and double bonds, and the benzene-ring bonds of 1,2-NQ were assumed to be 1.215, 1.49, 1.465, 1.35, and 1.40 Å, respectively.[1,2] All the valence angles in 1,2-NQ were assumed to be 120°.

TABLE 2. CALCULATED EXCITATION ENERGIES AND OSCILLATOR STRENGTHS OF THE SINGLET π, π^* EXCITED STATES AND THE CORRESPONDING $\pi\rightarrow\pi^*$ BANDS IN THE HEPTANE SOLUTION

Calculated				Observed	
No.	Angle (°)	E (eV)	f	Band name	E (eV)
1	106	4.320	0.077	I	3.3
2	124	4.486	0.091	II	3.7
3	67	5.286	0.587	III	5.0
6	99	5.953	0.425	IV	6.4
7	23	6.189	0.585		
13	151	7.215	0.417	V	7.3[a]
14	168	7.412	0.344		

a) This value is that of the HFP solution.

The n→π^* absorption band of 1,2-NQ is near 520 nm.[5] In Fig. 1, five $\pi\rightarrow\pi^*$ bands can be observed for the HFP solution. These $\pi\rightarrow\pi^*$ bands are denoted as Bands I-V, as is shown in Table 1. As is seen in Fig. 1, the intensity ratio of Band I to Band II in the HFP solution is very different from that in the heptane

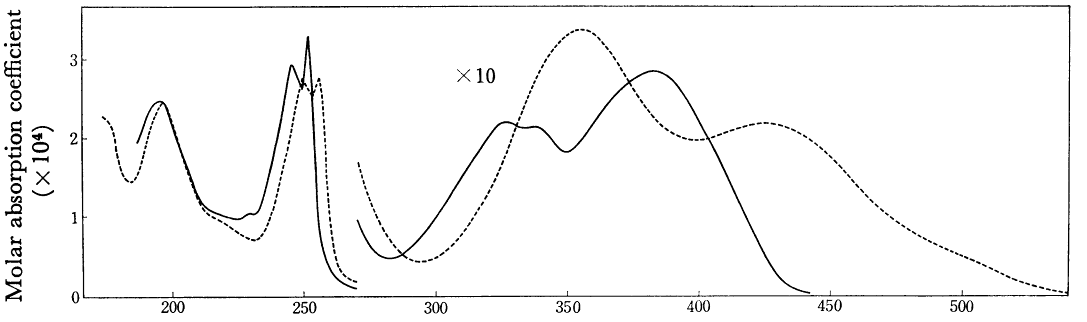


Fig. 1. Absorption spectra of 1,2-naphthoquinone in various solvents.
——: Heptane, ------: 1,1,1,3,3,3-hexafluoro-2-propanol.
In the heptane solution the scale of the ordinate is arbitrary.

solution and Bands I and II in the HFP solution show large red-shifts compared with those in the heptane solution. These facts may be due to the strong hydrogen-bond formation between 1,2-NQ and HFP.

In Table 2, the first column denotes an order based on the magnitude of the calculated excitation energies and the second column denotes the clockwise rotation angles of the directions of the transition moments with respect to the C(6)–C(7) bond axis. In this table, the data on the more highly-excited states with small *f*-values have been omitted. As may be seen in Table 2, the assignments of Bands I, II, and III based on the calculated results are reasonable, but those of Bands IV and V are not clear.

Table 3. The changes in the calculated excitation energy of the lowest π, π^* excited state of 1,2-NQ with alkyl-group substitutions at various positions

Position	ΔE (eV)[a]	Position	ΔE (eV)[a]
3	−0.067	6	+0.023
4	−0.018	7	−0.040
5	−0.043	8	−0.014

a) ΔE denotes the energy difference where the excitation energy of 1,2-NQ is subtracted from the corresponding energy for the substituted 1,2-NQ.

The changes in the calculated excitation energy of the lowest π,π^* excited states (state no. 1) with the alkyl-group substitutions are shown in Table 3. These calculations were carried out in the same manner as in previous works.[1,2] It is known that the methyl-group substitution at the 3-position of 1,2-NQ results in a relatively large red-shift of Band I.[6] In Table 3, the large energy decrease in the 3-position is consistent with this fact. In Table 3, the large energy increase in the 6-position is notable. Based on this result, a blue-shift of Band I of 6-alkyl-1,2-NQ compared with that of 1,2-NQ is expected. Since in 1,2-NQ the 6-position is the *para* position of the benzene nucleus with respect to the carbonyl group, this result is similar to that obtained for 9,10-phenanthrenequinone as reported in a previous paper.[2]

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