BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1874—1877 (1966)

The π-Electronic Excitation Energies of Anthraquinone

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(Received January 10, 1966)

Following our previous work on *o*-benzoquinone, the calculation of the π-electronic excitation energies of anthraquinone has been carried out with the Pariser-Parr-Pople method. The calculated excitation energies which correspond to the five distinct $\pi\rightarrow\pi^*$ bands have been obtained, though the agreement of the calculated excitation energies and the transition dipole-strengths with the observed energies and strengths are unsatisfactory. The π-electronic charge distribution in carbonyl groups of anthraquinone is almost the same as that of *p*-benzoquinone.

In our previous work,[1] the π-electronic excitation energies of *o*-benzoquinone were calculated using the Pariser-Parr-Popl method,[2,3] and from these results the $\pi\rightarrow\pi^*$ absorption bands of *o*-benzoquinone have been studied. In this paper, similar work on anthraquinone will be reported.

The Method of Calculation

The method of calculation was the same as that used in our previous work.[1] The integral values used have all been shown in our previous paper except for the core resonance integrals for carbon-carbon bonds.

The geometry of anthraquinone has been studied by Sen[4] by means of X-ray analysis. According to Sen's results, anthraquinone is planar, and its bond distances are as shown in Fig. 1.

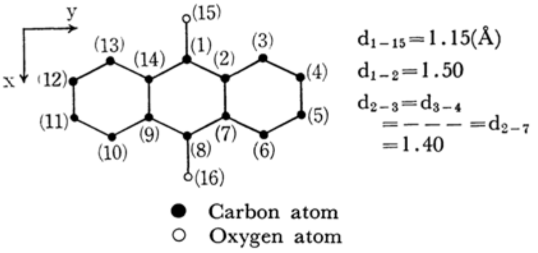

Fig. 1. Interatomic distances

In this work, these bond distances were used, and all the valence angles were assumed to be 120°. It was also assumed that anthraquinone is planar and that its symmetry group is D_{2h}.

As for the core resonance integral (β), the values of 1.45 eV. and 2.39 eV. were used for that over the atoms 1 and 2 and those of the benzene nuclei respectively, according to the method of Pariser and Parr.[2]

In the calculations, an electronic computor NEAC 2101 was used. The calculations were carried out in the same manner as in the previous work.[1]

Results

The molecular orbitals (ϕ_i) and their orbital energies (ε_i) are shown in Table I.[5] The excitation energies of the excited singlet and triplet configurations[6] less than 8 eV. are shown in Table II, along with the corresponding Coulomb and exchange integrals. Those of the orbitally-allowed and orbitally-forbidden transitions are shown in Table II (i) and II (ii) respectively.

The configuration interactions among the configurations in Table II were calculated. The obtained excited-state wave functions (${}^{1,3}\Phi_i$), their excitation energies (${}^{1,3}E_i-E_0$), the transition dipole-strengths from the ground state, and the interconfigurational matrix elements $(\Phi_{i\rightarrow j}|\mathbf{H}|\Phi_{k\rightarrow l})$ are shown in Table III.

In Table IV, the excitation energies, the transition dipole-strengths and the symmetry species of the excited states, experimentally determined,[7-9]

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1) A. Kuboyama and K. Wada, This Bulletin, **38**, 1709 (1965).

2) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

3) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

4) S. N. Sen, *Indian J. Phys.*, **22**, 347 (1948).

5) χ_i denotes the $2p\pi$ atomic orbital of *i*-atom.

6) Φ_0 and E_0 denote the wave function and the energy of the ground state respectively. ${}^1\Phi_{i\rightarrow j}$, ${}^1E_{i\rightarrow j}$ and ${}^3\Phi_{i\rightarrow j}$, ${}^3E_{i\rightarrow j}$ denote the wave functions and the energies of the singlet and triplet configurations, respectively, in which one electron is excited from an occupied orbital χ_i to an unoccupied orbital χ_j. The excitation energy of each excited configuration is given by the following formula.

$$\left.\begin{matrix}{}^1E_{i\rightarrow j}\\{}^3E_{i\rightarrow j}\end{matrix}\right\}-E_0=(E_j-E_i)-(J_{ij}-K_{ij})\left\{\begin{matrix}+K_{ij}\\-K_{ij}\end{matrix}\right.$$

J_{ij} and K_{ij} denote Coulomb and exchange integrals over ϕ_i and ϕ_j respectively.

7) K. P. Popov and L. V. Smirnov, *Optics & Spectroscopy*, **13**, 155 (1962).

8) H. Labhart, *Chimia*, **15**, 20 (1961).

9) A. Kuboyama, Preprints of the International Conference on Photochemistry, Tokyo, p. 117 (1965) (The results obtained from the dichroism of phosphorescence excitation spectra.).

TABLE I. SCF MO'S AND THEIR ENERGIES

Symmetry	SCF MO's	Orbital energies, eV.
b_{1u}	$\phi_1=0.4145\psi_1+0.6297\psi_2+0.4439\psi_3+0.3578\psi_4+0.3263\psi_5$	−13.818
b_{3g}	$\phi_2=0.5872\psi_6+0.5738\psi_7+0.5708\psi_8$	−13.144
b_{2g}	$\phi_3=0.6554\psi_9+0.2321\psi_{10}+0.1696\psi_{11}+0.0691\psi_{12}+0.6949\psi_{13}$	−12.326
b_{1u}	$\phi_4=0.4709\psi_1-0.0106\psi_2-0.3608\psi_3-0.5840\psi_4+0.5537\psi_5$	−11.964
b_{3g}	$\phi_5=0.7026\psi_6-0.0114\psi_7-0.7113\psi_8$	−9.934
a_u	$\phi_6=0.4210\psi_{14}+0.8125\psi_{15}+0.4031\psi_{16}$	−9.907
b_{2g}	$\phi_7=0.1066\psi_9-0.3744\psi_{10}-0.7907\psi_{11}-0.3962\psi_{12}+0.2569\psi_{13}$	−9.802
b_{1u}	$\phi_8=0.1808\psi_1-0.6460\psi_2-0.0538\psi_3+0.6003\psi_4+0.4318\psi_5$	−9.551
b_{2g}	$\phi_9=0.3567\psi_9+0.6119\psi_{10}-0.1288\psi_{11}-0.5217\psi_{12}-0.4575\psi_{13}$	0.546
b_{1u}	$\phi_{10}=0.2482\psi_1+0.3083\psi_2-0.7750\psi_3+0.3971\psi_4-0.2913\psi_5$	1.166
a_u	$\phi_{11}=0.7190\psi_{14}-0.0280\psi_{15}-0.6944\psi_{16}$	1.297
b_{3g}	$\phi_{12}=0.4017\psi_6-0.8188\psi_7+0.4099\psi_8$	1.404
b_{2g}	$\psi_{13}=0.5374\psi_9-0.1685\psi_{10}-0.3059\psi_{11}+0.6299\psi_{12}-0.4385\psi_{13}$	3.073
b_{1u}	$\psi_{15}=0.7155\psi_1-0.3014\psi_2+0.2628\psi_3-0.1123\psi_4-0.5616\psi_5$	3.179
a_u	$\psi_{15}=0.5529\psi_{14}-0.5822\psi_{15}+0.5960\psi_{16}$	4.572
b_{2g}	$\psi_{16}=0.3780\psi_9-0.6347\psi_{10}+0.4854\psi_{11}-0.4112\psi_{12}-0.2221\psi_{13}$	5.155

$$\psi_1=\frac{1}{\sqrt{2}}(\chi_1+\chi_8) \qquad \psi_9=\frac{1}{\sqrt{2}}(\chi_1-\chi_8)$$

$$\psi_2=\frac{1}{2}(\chi_2+\chi_7+\chi_9+\chi_{14}) \qquad \psi_{10}=\frac{1}{2}(\chi_2-\chi_7-\chi_9+\chi_{14})$$

$$\psi_3=\frac{1}{2}(\chi_3+\chi_6+\chi_{10}+\chi_{13}) \qquad \psi_{11}=\frac{1}{2}(\chi_3-\chi_6-\chi_{10}+\chi_{13})$$

$$\psi_4=\frac{1}{2}(\chi_4+\chi_5+\chi_{11}+\chi_{12}) \qquad \psi_{12}=\frac{1}{2}(\chi_4-\chi_5-\chi_{11}+\chi_{12})$$

$$\psi_5=\frac{1}{\sqrt{2}}(\chi_{15}+\chi_{16}) \qquad \psi_{13}=\frac{1}{\sqrt{2}}(\chi_{15}-\chi_{16})$$

$$\psi_6=\frac{1}{2}(\chi_2+\chi_7-\chi_9-\chi_{14}) \qquad \psi_{14}=\frac{1}{2}(\chi_2-\chi_7+\chi_9-\chi_{14})$$

$$\psi_7=\frac{1}{2}(\chi_3+\chi_6-\chi_{10}-\chi_{13}) \qquad \psi_{15}=\frac{1}{2}(\chi_3-\chi_6+\chi_{10}-\chi_{13})$$

$$\psi_8=\frac{1}{2}(\chi_4+\chi_5-\chi_{11}-\chi_{12}) \qquad \psi_{16}=\frac{1}{2}(\chi_4-\chi_5+\chi_{11}-\chi_{12})$$

TABLE II. EXCITATION ENERGIES AND TRANSITION DIPOLE-STRENGTHS OF THE CONFIGURATIONS AND ELECTRON REPULSION INTEGRALS

$i\rightarrow j$	Symmetry	${}^1E_{i\rightarrow j}$-E_0, eV.	μ^2, Å^2	${}^3E_{i\rightarrow j}$-E_0, eV.	J_{ij}, eV.	K_{ij}, eV.
(i) Orbitally allowed transitions						
8→ 9	B_{3u}	6.144	1.655	4.983	5.114	0.580
6→ 9	B_{2u}	6.153	0.999	5.738	4.716	0.208
8→12	B_{2u}	6.691	0.946	6.247	4.708	0.222
7→11	B_{2u}	6.820	1.061	6.309	4.792	0.255
5→10	B_{2u}	6.836	1.106	5.366	4.734	0.235
7→10	B_{3u}	6.959	0.519	6.096	4.873	0.431
5→11	B_{3u}	7.154	0.490	6.042	5.190	0.556
6→12	B_{3u}	7.341	0.972	6.302	5.010	0.520
(ii) Orbitally forbidden transitions						
5→ 9	B_{1g}	6.083		5.538	4.942	0.272
7→ 9	A_g	6.225		5.600	4.749	0.312
8→11	B_{1g}	6.498		5.840	5.009	0.329
8→10	A_g	6.605		5.981	4.736	0.312
6→11	A_g	7.133		6.345	4.861	0.394
6→10	B_{1g}	7.206		6.173	4.901	0.517
5→12	A_g	7.264		6.507	4.831	0.379
7→12	B_{1g}	7.360		6.268	4.939	0.546

TABLE III. WAVE FUNCTIONS, EXCITATION ENERGIES AND TRANSITION DIPOLE-STRENGTHS OF EXCITED STATES AND INTERCONFIGURATIONAL MATRIX ELEMENTS

(1) Singlet states

Symmetry		${}^{1,3}E_i$-E_0, eV.	μ^2, Å^2
B_{3u}	${}^1\Phi_1=0.3768\,{}^1\Phi_{8\to9}+0.5294\,{}^1\Phi_{6\to12}+0.6362\,{}^1\Phi_{7\to10}+0.4158\,{}^1\Phi_{5\to11}$	4.020	0.007
B_{2u}	${}^1\Phi_2=0.4722\,{}^1\Phi_{8\to12}-0.5912\,{}^1\Phi_{6\to9}+0.4493\,{}^1\Phi_{5\to10}-0.4750\,{}^1\Phi_{7\to11}$	4.849	0.022
B_{2u}	${}^1\Phi_3=0.5593\,{}^1\Phi_{8\to12}+0.6094\,{}^1\Phi_{6\to9}+0.4952\,{}^1\Phi_{5\to10}+0.2658\,{}^1\Phi_{7\to11}$	6.367	3.792
B_{3u}	${}^1\Phi_4=0.9134\,{}^1\Phi_{8\to9}-0.2667\,{}^1\Phi_{6\to12}-0.3068\,{}^1\Phi_{7\to10}-0.0188\,{}^1\Phi_{5\to11}$	6.460	2.171
B_{2u}	${}^1\Phi_5=0.0177\,{}^1\Phi_{8\to12}+0.5179\,{}^1\Phi_{6\to9}-0.2128\,{}^1\Phi_{5\to10}-0.8284\,{}^1\Phi_{7\to11}$	7.490	0.294
B_{3u}	${}^1\Phi_6=0.1492\,{}^1\Phi_{8\to9}+0.4598\,{}^1\Phi_{6\to12}+0.0976\,{}^1\Phi_{7\to10}-0.8699\,{}^1\Phi_{5\to11}$	7.657	1.423
B_{2u}	${}^1\Phi_7=0.6811\,{}^1\Phi_{8\to12}-0.1040\,{}^1\Phi_{6\to9}-0.7125\,{}^1\Phi_{5\to10}+0.1325\,{}^1\Phi_{7\to11}$	7.794	0.003
B_{3u}	${}^1\Phi_8=0.0370\,{}^1\Phi_{8\to9}-0.6611\,{}^1\Phi_{6\to12}+0.7011\,{}^1\Phi_{7\to10}-0.2645\,{}^1\Phi_{5\to11}$	9.462	0.005
A_g	${}^1\Phi_9=0.7716\,{}^1\Phi_{7\to9}-0.1461\,{}^1\Phi_{8\to10}+0.6020\,{}^1\Phi_{6\to11}-0.1440\,{}^1\Phi_{5\to12}$	4.902	Forbidden
A_g	${}^1\Phi_{10}=0.1693\,{}^1\Phi_{7\to9}+0.7512\,{}^1\Phi_{8\to10}+0.1154\,{}^1\Phi_{6\to11}+0.6274\,{}^1\Phi_{5\to12}$	5.087	Forbidden
B_{1g}	${}^1\Phi_{11}=0.7875\,{}^1\Phi_{5\to9}+0.1037\,{}^1\Phi_{6\to10}+0.6007\,{}^1\Phi_{8\to11}+0.0902\,{}^1\Phi_{7\to12}$	5.492	Forbidden
B_{1g}	${}^1\Phi_{12}=0.1172\,{}^1\Phi_{5\to9}-0.7314\,{}^1\Phi_{6\to10}+0.0728\,{}^1\Phi_{8\to11}-0.6678\,{}^1\Phi_{7\to12}$	6.456	Forbidden

(2) Triplet states

B_{3u}	${}^3\Phi_1=0.6812\,{}^3\Phi_{8\to9}+0.3788\,{}^3\Phi_{6\to12}+0.4244\,{}^3\Phi_{7\to10}+0.4608\,{}^3\Phi_{5\to11}$	3.847
B_{1g}	${}^3\Phi_1=0.5123\,{}^3\Phi_{5\to9}+0.5209\,{}^3\Phi_{6\to10}+0.4583\,{}^3\Phi_{8\to11}+0.5061\,{}^3\Phi_{7\to12}$	4.200
A_g	${}^3\Phi_3=0.6495\,{}^3\Phi_{7\to9}+0.4570\,{}^3\Phi_{8\to10}+0.4874\,{}^3\Phi_{6\to11}+0.3629\,{}^3\Phi_{5\to12}$	4.323
B_{1g}	${}^3\Phi_4=0.5413\,{}^3\Phi_{5\to9}-0.4910\,{}^3\Phi_{6\to10}+0.4841\,{}^3\Phi_{8\to11}-0.4811\,{}^3\Phi_{7\to12}$	4.447
B_{3u}	${}^3\Phi_5=0.4673\,{}^3\Phi_{8\to9}-0.5756\,{}^3\Phi_{6\to12}-0.5877\,{}^3\Phi_{7\to10}-0.3237\,{}^3\Phi_{5\to11}$	4.506
B_{2u}	${}^3\Phi_6=0.2990\,{}^3\Phi_{8\to12}+0.7041\,{}^3\Phi_{6\to9}+0.2912\,{}^3\Phi_{5\to10}+0.5744\,{}^3\Phi_{7\to11}$	4.556

(3) Interconfigurational matrix elements

	Singlet state, eV.	Triplet state, eV.
$(\Phi_{8\to12}\vert\mathbf{H}\vert\Phi_{6\to9})$	0.333	−0.091
$(\Phi_{8\to12}\vert\mathbf{H}\vert\Phi_{5\to10})$	−1.019	−1.471
$(\Phi_{8\to12}\vert\mathbf{H}\vert\Phi_{7\to11})$	0.453	−0.023
$(\Phi_{6\to9}\vert\mathbf{H}\vert\Phi_{5\to10})$	0.385	−0.043
$(\Phi_{6\to9}\vert\mathbf{H}\vert\Phi_{7\to11})$	−0.928	−1.379
$(\Phi_{5\to10}\vert\mathbf{H}\vert\Phi_{7\to11})$	0.387	−0.100
$(\Phi_{8\to9}\vert\mathbf{H}\vert\Phi_{6\to12})$	−0.478	−0.091
$(\Phi_{8\to9}\vert\mathbf{H}\vert\Phi_{7\to10})$	−0.490	−0.275
$(\Phi_{8\to9}\vert\mathbf{H}\vert\Phi_{5\to11})$	−0.567	−1.350
$(\Phi_{6\to12}\vert\mathbf{H}\vert\Phi_{7\to10})$	−2.160	−1.903
$(\Phi_{6\to12}\vert\mathbf{H}\vert\Phi_{5\to11})$	−0.491	−0.130
$(\Phi_{7\to10}\vert\mathbf{H}\vert\Phi_{5\to11})$	−1.304	−0.100

TABLE IV. THE OBSERVED ABSORPTION BANDS OF ANTHRAQUINONE

	Excitation energy, eV.	μ^2, Å^2	Symmetry
Band I	3.8	~0.3	${}^1B_{3u}$
Band II	4.5	~0.7	${}^1B_{2u}$
Band III	4.9	~1.8	${}^1B_{3u}$
Band IV	6.1	~0.7	?
Band V	~6.7	>0.7	?

of the observed $\pi\to\pi^*$ absorption bands (I-V) of anthraquinone are shown.10) The direction of the polarization of the transitions (${}^1A_g\to{}^1B_{3u}$, ${}^1A_g\to{}^1B_{2u}$) are along the x and y axes in Fig. 1 respectively.

In Fig. 2(a) the π-electronic charge densities and π-bond orders of anthraquinone obtained are

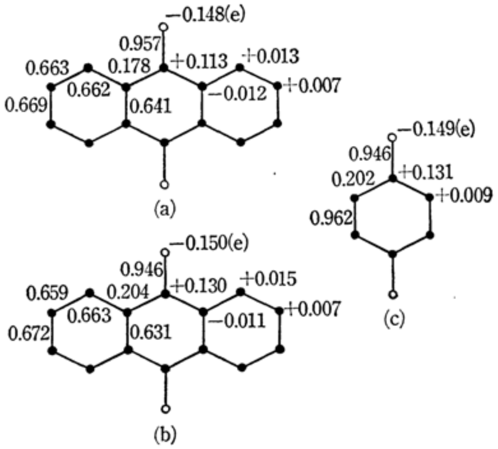

Fig. 2. Molecular diagrams.

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10) Anthraquinone has an $n\to\pi^*$ band near 400 mμ.

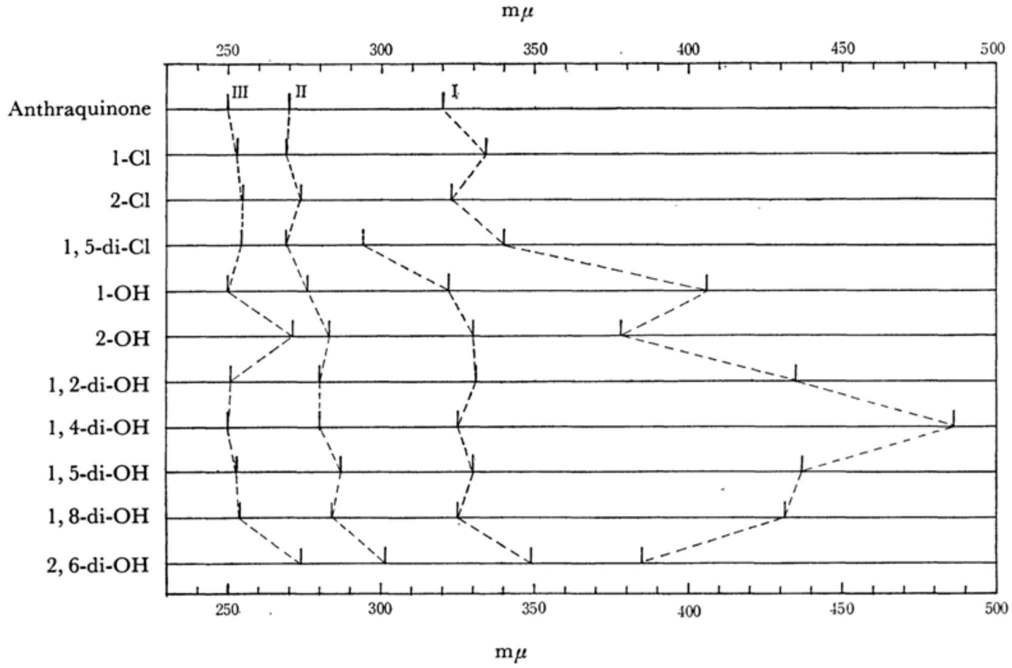

Fig. 3. Correspondence among $\pi\rightarrow\pi^*$ bands of anthraquinone and its chlorine or hydroxyl substitutes.

shown, while Fig. 2(b) shows those obtained using as the core resonance integral over the atoms 1 and 2 the value (1.68 eV.) which corresponds to the bond distance (1.47 Å). In Fig. 2(c) those of *p*-bnezoquinone calculated using the wave functions obtained by Sidman[11] are shown.

Discussion

Since all the intensities of Bands II—V in Table IV are strong, these absorption bands may reasonably be assigned to $\pi\rightarrow\pi^*$ allowed transitions. As for Band I, its intensity is not weak and it has a sharp peak at the longest wavelength edge in saturated hydrocarbons. Therefore, Band I may also reasonably be assigned to an allowed transition. From a comparison of Tables III and IV, Bands II and III may reasonably be assigned to the $E_0\rightarrow{}^1E_3$ $({}^1A_g\rightarrow{}^1B_{2u})$ and $E_0\rightarrow{}^1E_4$ $({}^1A_g\rightarrow{}^1B_{3u})$ transitions respectively. Bands IV and V may also reasonably be assigned to either one of the two transitions $(E_0\rightarrow{}^1E_5$ $({}^1A_g\rightarrow{}^1B_{2u})$ and $E_0\rightarrow{}^1E_6$ $({}^1A_g\rightarrow{}^1B_{3u}))$. Band I may be assigned to the $E_0\rightarrow{}^1E_1$ $({}^1A_g\rightarrow{}^1B_{3u})$, transition though the calculated dipole-strength of this transition is too small in comparison with that of Band I. The absorption band due to the $E_0\rightarrow{}^1E_2$ $({}^1A_g\rightarrow{}^1B_{2u})$ transition may be hidden in Band I. α- or β-Hydroxy-anthraquinone[12] has an absorption band between Bands I and II the intensity of which is nearly equal to that of Band I. This absorption band may be assigned to the $E_0\rightarrow{}^1E_2$ transition. $\pi\rightarrow\pi^*$ bands of anthraquinone and its various chlorine[13] or hydroxyl[12] substitutes at the wavelengths longer than 240 mμ reasonably correspond to each other, as shown in Fig. 3. Those of various amino-anthraquinones[14] also correspond to those of the corresponding hydroxy-anthraquinones in Fig. 3 respectively.

The calculated singlet excitation energies of anthraquinone are much greater than the observed ones. A similar trend was observed in the *o*-[1] and *p*-benzoquinone[11] studied previously. In anthraquinone the agreement between the transition dipole-strengths calculated and those observed is also unsatisfactory. The alternate use of 1.68 eV. in place of 1.45 eV. as the core resonance integral over the atoms 1 and 2, or the use of -14.00 eV. in place of -13.00 eV. as U_{oo},[1] does not bring about any essential improvement in these points.

In Fig. 2 the charge distribution in carbonyl groups of anthraquinone is similar to those in *p*-benzoquinone and o-benzoquinone shown in our previous paper.[1] Especially it almost agrees with that in *p*-benzoquinone.

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[11] J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

[12] R. A. Morton and W. T. Earlam, *J. Chem. Soc.*, **1941**, 159. The solvent used was ethanol except for the case of 1, 4-dihydroxy-anthraquinone where hexane was used. The absorption-peak wavelengths of hydroxy-anthraquinones in ethanol and hexane are similar to each other.

[13] A. Kuboyama, unpublished work. The solvent used was *n*-heptane except for the case of 1, 4-dichloro-anthraquinone where methylcyclohexane was used.

[14] H. Hartmann and E. Lorenz, *Z. Naturforsh.*, **7b**, 360 (1952).