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The CNDO/S-CI Calculations of the Singlet $n\pi^*$ and $\pi\pi^*$ Levels of Quinones

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Synopsis. The calculations proved to reproduce well the observed S_1 $n\pi^*$ levels of quinones, the numbers of the singly excited configurations contained in CI being twice those of the basis AO's. The calculations taking 0.500 as the κ value reproduce well the observed singlet $\pi\pi^*$ levels also. The unknown S_1 $n\pi^*$ levels of some quinones were predicted on the basis of the calculated results.

As for the CNDO/S-CI[1)] calculations of the singlet electronic-energy levels of quinones, only a few works[2)] on *p*-quinones have been reported. In this work, the lowest-energy singlet $n_\pm\pi^*$[3)] levels of principal *o*- and *p*-quinones have been studied with the aid of the CNDO/S-CI calculations. In the calculations, two κ values,[4)] 0.585 (the formal one) and 0.500, were used. The 0.500 value was chosen to reproduce the observed energy difference between the $n_\pm\pi^*$ levels of *p*-benzoquinone, as will be shown later. In this work, the calculations using the two κ values are called as Cals. A and B respectively. The geometries of the quinones used in the calculations were the same as those used in the previous works,[5)] except for that of *o*-benzoquinone, where the C–H bond length was taken as 1.084 Å. In *o*-benzoquinone[6)] and acenaphthenequinone,[7)] those values determined by X-ray-crystal analysis were used. Those of 2,6-naphthoquinone and diphenoquinone, and that of 5,14:7,12-pentacenediquinone, were determined on the basis of those of *p*-benzoquinone and 9,10-anthraquinone respectively.

In Fig. 1, n in the abscissa denotes the ratio of the number of the lowest singly excited configurations included in the calculations (Cal. A) to that of the basis AO's in the MO's. As may be seen in Fig. 1, in *p*-benzoquinone the lowest $n_+\pi^*$ levels is higher than the lowest $n_-\pi^*$ level, and the energy separation (ΔE) between them is of the order of 0.1 eV, while in *o*-benzoquinone the $n_-\pi^*$ level is higher than the $n_+\pi^*$ level and the ΔE is of the order of 1 eV, as in α-diketones.[8)] In both quinones, the $n_\pm\pi^*$ levels become lower with the increase in n, but, broadly speaking,

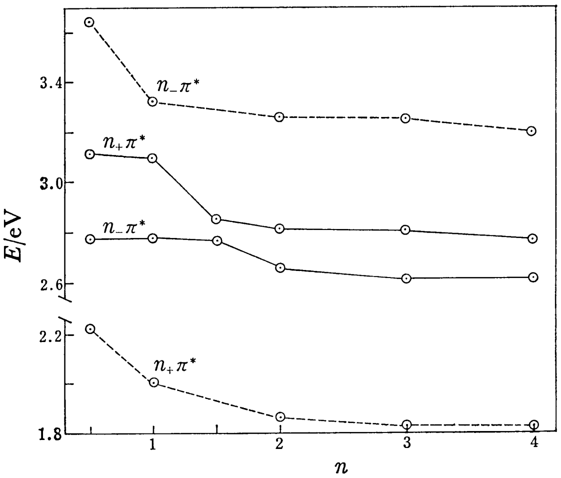

Fig. 1. The lowest singlet $n_\pm\pi^*$ levels of benzoquinones obtained by Cal. A. As for n in the abscissa, see Text.
——: *p*-Benzoquinone, ----: *o*-benzoquinone.

Table 1. Calculated singlet $n\pi^*$ levels of quinones

	Cal. A			Cal. B		Obsd[9)]
	S_1		ΔE[a)]	S_1	ΔE[a)]	E
	Symmetry	E/eV	eV	E/eV	eV	eV
(1) *p*-Quinones						
p-Benzoquinone	B_{1g}	2.659	0.153	2.582	0.023	2.48
1,4-Naphthoquinone	B_1	2.749	0.082	2.601	0.008	2.68
9,10-Anthraquinone	B_{1g}	2.918	0.199	2.742	0.140	2.92
2,6-Naphthoquinone	A_u	2.826	0.029	2.674	0.035	
Diphenoquinone	B_{1g}	2.863	0.049	2.766	0.015	
5,14 : 7,12-Pentacenediquinone	B_{3u}	3.015	0.102[b)]	2.926	0.049[b)]	
(2) *o*-Quinones						
o-Benzoquinone	B_1	1.866	1.393	1.878	1.069	1.91[c)]
1,2-Naphthoquinone	(B_1)	2.183	1.162	2.130	0.898	2.19
9,10-Phenanthrenequinone	B_1	2.408	1.139	2.308	0.896	2.38
Biphenylene-2,3-dione	B_1	2.357	1.173	2.229	0.951	2.25
Acenaphthenequinone	B_1	2.567	0.928	2.471	0.773	2.42

a) The S_1 levels in *p*- and *o*-quinones are the $n_-\pi^*$ and $n_+\pi^*$ levels respectively. b) The energy difference between the S_1 and S_2 $n\pi^*$ levels. c) The estimated value.

settle at the point (n=2). Similar results were obtained in other *o*- and *p*-quinones. Results similar to the above were also obtained in Cal. B. Therefore, only the calculated values in the (n=2) case are used below.

In Table 1, the S_1–S_0 transitions are all found to be allowed transitions (out-of-plane) except for those of the three D_{2h}-type *p*-quinones, such as *p*-benzoquinone. It is also found that the S_1 level of each quinone is a little higher in Cal. A than in Cal. B, except for that of *o*-benzoquinone, and that in both Cals. A and B it is generally in good agreement with the observed one. The observed values are those of the longest-wavelength peaks or shoulders[9] of the S–S $n\pi^*$ absorption spectra in saturated hydrocarbon solutions.

As for ΔE, in Table 1 it is smaller in Cal. B than in Cal. A in each quinone except for 2,6-naphthoquinone. In *p*-benzoquinone, the observed values (0.032[10]—0.0004[11]) eV (crystal) and 0.007 eV(gas)[12]) are close to that in Cal. B. As the observed energy separations between the triplet $n_\pm\pi^*$ levels of 9,10-anthraquinone[13] are not far from those of *p*-benzoquinone, the ΔE of 9,10-anthraquinone may be expected to be not far from that of *p*-benzoquinone. It is noticeable that the ΔE of 9,10-anthraquinone in Cal. B is considerably larger than that of *p*-benzoquinone. It is, however, uncertain at this stage whether or not this difference is significant.[14] In consideration of the large ΔE values of the *o*-quinones in Table 1, the S–S $n\pi^*$ absorption spectra of *o*-quinones may be concluded to consist of the $n_+\pi^*$ absorption spectra alone, as in α-diketones.[8]

TABLE 2. CALCULATED LOW-ENERGY SINGLET $\pi\pi^*$ LEVELS OF QUINONES

	Cal. A		Cal. B	Obsd[5]
	Symmetry	E/eV	E/eV	E/eV
p-Benzoquinone	B_{3g}	4.909	4.394	4.5
	B_{1u}	5.767	5.225	5.2
1,4-Naphthoquinone	A_1	4.376	3.804	3.8
	B_2	4.624	4.116	
	B_2	5.472	4.866	5.1
	A_1	5.739	5.199	
9,10-Anthraquinone[a]	B_{2u}	4.413	3.828	3.9
	B_{1u}	5.330	4.803	4.6
	B_{2u}	5.571	4.959	5.0
o-Benzoquinone	B_2	3.799	3.440	3.5
1,2-Naphthoquinone		3.969	3.545	3.3
		4.367	3.836	3.7
		5.258	4.922	5.0
9,10-Phenanthrenequinone	B_2	3.917	3.475	3.1
	A_1	4.377	3.799	3.9
	B_2	4.477	3.949	3.7
	B_2	5.197	4.681	4.8
	A_1	5.458	4.887	

a) The forbidden levels have been omitted.

The low-energy $\pi\pi^*$ levels of the principal *o*- and *p*-quinones[5] obtained by Cal. B are found to be in good agreement with the observed ones in saturated hydrocarbon solutions, as may be seen in Table 2. The $n\pi^*$ S–S absorption spectra of 2,6-naphthoquinone and diphenoquinone have never been reported. In these quinones, as the lowest-singlet $\pi\pi^*$ levels are higher by 0.92 and 0.50 eV than the S_1 $n_-\pi^*$ levels respectively in Cal. B, the S_1 state may be predicted to be the $n_-\pi^*$ state. In addition, the S_1–S_4 states of 5,14:7,12-pentacenediquinone are all the $n\pi^*$ states (the B_{3u}, B_{1g}, A_u, and B_{3g} states respectively) in both Cals. A and B, where the ΔE's between S_1 and S_4 levels obtained by Cals. A and B are 0.320 and 0.195 eV respectively.

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3) In $n_\pm\pi^*$, $n_\pm$ denote the symmetric and anti-symmetric linear combinations of the two oxygen lone-pair orbitals, n_1 and n_2, of quinones respectively, and π^*, the lowest-energy π^* orbital. In quinones, this π^* orbital usually contains an anti-symmetric linear combination of the two carbonyl parts.

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