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Visible Absorption Spectra of Aryl-*p*-Benzoquinones by Modified PPP MO Calculation

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ABSTRACT

*Colour and constitution of aryl-*p*-benzoquinones were evaluated by means of the modified PPP MO method with variable β,γ approximation. Introduction of electron-withdrawing groups such as halogeno and cyano into the quinone ring produced a large bathochromic shift of the first absorption maximum (λ_{max}). Steric hindrance between the quinone ring and the 2-aryl group was increased with 2'-substitution in the 2-aryl group, and, whilst causing a decrease in ε, hardly affected λ_{max}. The strong intramolecular charge-transfer character of the first absorption band was evaluated, and the substituent effects were well reproduced by the calculated results.*

1 INTRODUCTION

Colour and constitution determinations of organic colorants by means of the PPP MO method has been summarized by Griffiths,[1,2] and Fabian and Hartmann.[3] The modified PPP MO method has so far been applied systematically to study the absorption spectra of azobenzenes,[4] anthraquinones,[5,6] and 1,4-naphthoquinones.[7] However, few calculations by means of the modified PPP MO method with variable β,γ approximation have been reported for aryl-*p*-benzoquinones. The basic chromophoric systems of substituted *p*-benzoquinones have been evaluated previously.[7]

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In our earlier work, a new series of aryl-*p*-benzoquinone dyes were synthesized and their absorption spectra in solution reported.[8]

In this paper, the colour and constitution of these dyes are studied by means of the modified PPP MO method with improved parameterizations. Solvent effects and ^{1}H NMR spectra were evaluated to ascertain the steric hindrance between the quinone and 2-aryl group.

2 MO CALCULATION

2.1 Calculation method

Calculations were carried out by means of the PPP MO method[9,10] with variable β,γ approximation.[11]

The core-resonance integral (β_{rs}) and the bond lengths (R_{rs}) were adjusted at every iteration of the SCF calculations in accordance with the following equations;

$$\beta_{CC} = -2{\cdot}04 - 0{\cdot}510 \times P_{CC}$$
$$\beta_{CN} = -2{\cdot}24 - 0{\cdot}530 \times P_{CN}$$
$$\beta_{CO} = -2{\cdot}44 - 0{\cdot}560 \times P_{CO}$$
$$R_{CC} = 1{\cdot}517 - 0{\cdot}180 \times P_{CC}$$
$$R_{CN} = 1{\cdot}451 - 0{\cdot}180 \times P_{CN}$$
$$R_{CO} = 1{\cdot}410 - 0{\cdot}180 \times P_{CO}$$

where P_{rs} is the π-bond order between atom r and s.

The two-centre repulsion integrals (γ_{rs}) were calculated by means of the Nishimoto–Mataga equation.[12] Valence-state ionization potentials (VSIP), one-centre repulsion integrals (γ_{rr}) and other parameters used are given in Table 1, together with the references. The evaluations of the parameters in this work are described in the following section.

2.2 Configuration interaction

The dependence of the calculated first excitation energy (ΔE_1) on the numbers of orbital for configuration interactions were examined by using 2-[4'-(dimethylamino)phenyl]-*p*-benzoquinone (**1a**) as a model planar compound. The results are given in Fig. 1, with two sets of parameters for the hetero atoms. The calculated ΔE_1 values decrease in accord with increment of the numbers of CI orbitals, and converge after 25 orbitals. Consequently, a reasonable number of orbitals for the configuration interaction was decided to be 25, and singly excited configurations associated with the transitions are considered.

TABLE 1
PPP MO Calculation Parameters

Bond X—Y	β_{xy} *(eV)*	*Bond length*	*VSIP (Y) (eV)*	γ_{yy} *(eV)*	*Core charge (Y)*	*Ref.*
C=C (aromatic)	VB	VB	11·16	11·13	1·0	4, 13
=C—C (olefinic)	VB	VB	11·16	11·13	1·0	13
CC—F	−1·80	1·30	30·00 39·00[a]	21·00	2·0	14
CC—Cl	−1·36	1·74	23·30 30·29[a]	10·80	2·0	14
C=O (acetyl)	VB	VB	17·70	15·23	1·0	5
C=O (ester)	VB	VB	17·70	15·23	1·0	5
CO—O (ester)	VB	VB	35·00	21·53	2·0	4
C—N (nitrile)	−2·675	VB	14·18	10·68	1·0	4, 15
N—C (nitrile)	−2·675	VB	11·19 14·55[a]	11·09	1·0	4, 15
C—NMe_2	VB	VB	25·50[b] 24·50[c]	17·44	2·0	4, 5
C—NEt_2	VB	VB	24·90[b] 23·90[c]	17·44	2·0	4, 5
C—OMe (quinone)	VB	VB	37·00	21·47	2·0	13
C—OMe (benzene)	VB	VB	35·00	21·53	2·0	5

[a] New parameters in this work. Calculations were conducted by using these parameters for halogeno and cyano dyes (Table 2).
[b] Parameters for nonpolar solvent such as C_6H_{12}.
[c] Parameters for polar solvent such as EtOH.

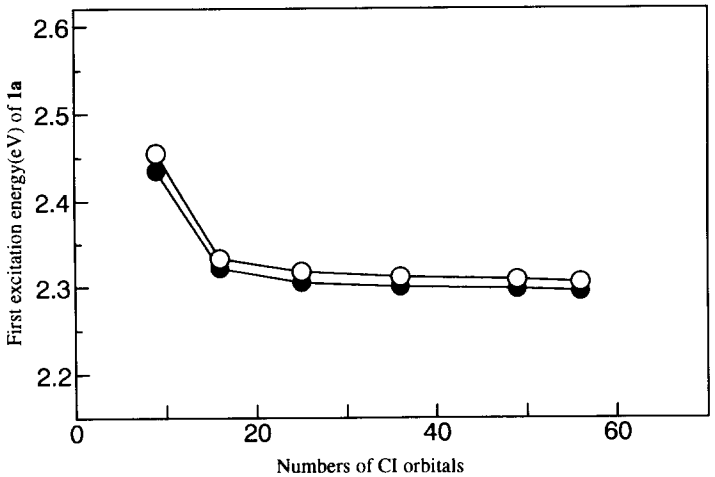


Fig. 1. Relationship between the first excitation energy on numbers of CI orbitals with two sets (A and B) of parameters.

2.3 Parameterization of dye 1 in planar geometry

In general, the first excitation energy depends largely on the VSIP (or electron affinity) of the atoms, and the parameters (VSIP, γ, etc) of the hetero atoms (except for carbon atoms) are then usually estimated on the basis of observed or reported values of analogous compounds. The parent compound **1a** has two hetero atoms, viz., the O atom of the carbonyl group and the N atom of the dialkylamino group, and their VSIP (and γ) values are evaluated for parameterization. The Electron affinity (E_A) is defined by eqn (1).

$$E_A = IP - \gamma_{rr} \tag{1}$$

The two values of electron affinities for the O atom (2·50 and 2·47 eV) and of the N atom (8·05 and 7·86 eV) used in Fig. 1 are very similar. The calculated first excitation energies obtained by using those two sets of different parameters were approximately the same, as shown in Fig. 1. Thus, in the present calculations, parameter set A was employed and these values have been used in the variable β,γ approximation method. A good linear relationship between the calculated ΔE_1 of **1a** and the VSIP values of the N atom is shown in Fig. 2, which indicates that the electron-donating properties of various substituents can be decided from the VSIP

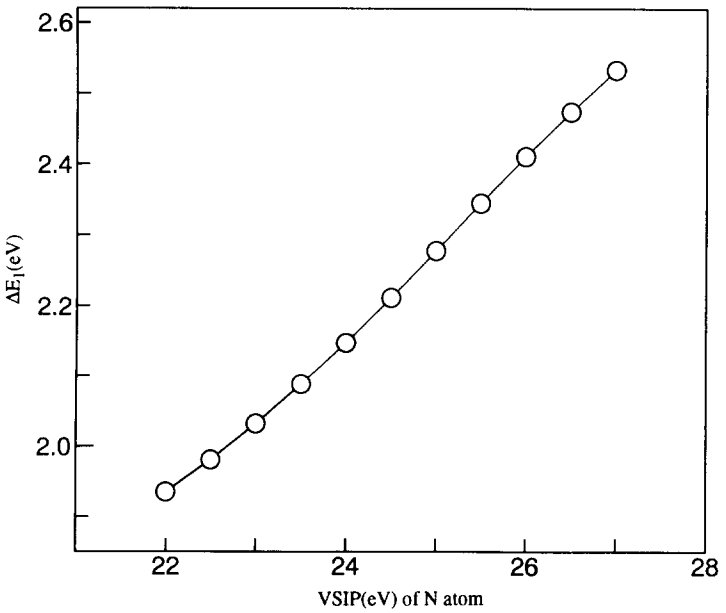


Fig. 2. Relationship between the calculated first excitation energy (ΔE_1) on VSIP(eV) of N atom in dye (**1a**).

values shown in the figure. In accordance with the observed and the calculated first absorption maximum (λ_1) value, the values of 25·50 eV for the dimethylamino group (**1a**) and 24·90 eV for the diethylamino group (**1b**) were used, respectively, in this work.

2.4 Parameterization of dyes 2 in nonplanar geometry

Two conformational isomers of **2a** in the planar geometry shown in Fig. 3 were considered for calculation. The calculated absorption maxima (λ_1) for conformers A and B were 575 nm and 606 nm, respectively. Structure A is more favourable than B from comparison of the λ_1 value with the observed value (λ_{max}).

From their spectral properties, dyes **1** will be planar, but dyes **2** are not planar because of steric hindrance between the 2'-methoxy group and the quinone ring substituent.[13] In fact, the molar extinction coefficients of **2a** and **2b** were much smaller than those of the corresponding **1a** and **1c**, respectively. On the other hand, the observed λ_{max} values of **2a** and **2b** were approximately the same as those of **1a** and **1c**, in spite of the presence of the electron-donating 2'-methoxy group (Table 2).

The core-resonance integral, $\beta_{rs}(\theta)$, for a twisted bond is generally rationalized by the following equation,[4,5]

$$\beta_{rs}(\theta) = \beta_{rs}(0) \times \cos(\theta)$$

where θ denotes the degree of twist angle of the bond against the nonplanar geometry and $\beta_{rs}(0)$ is the core-resonance integral in a planar situation. The effect of the twist angle around the bonds (a) and (b) in Fig. 3 on the $\lambda_1(\Delta E_1)$ of **2a** was examined and the results are shown in Table 3. In the case of bond (a), λ_1 shifted to longer wavelength in accord with the increment of the twist angle. Such a bathochromic shift has been reported for azo dyes with intramolecular charge-transfer chromophoric systems.[4]

In contrast, hypsochromic shifts were calculated according to increment of the twist angle around bond (b). In this case, the twist of bond (b) was

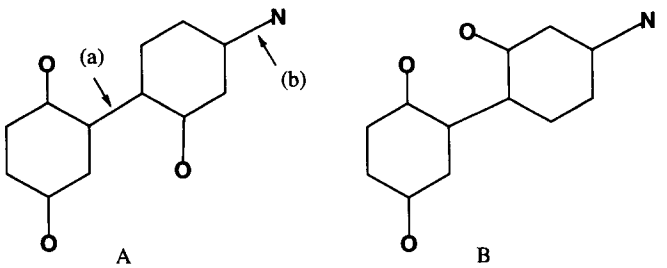
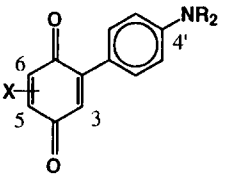
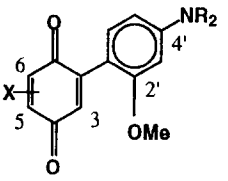


Fig. 3. Two conformational isomers of **2a**.

TABLE 2
Visible Absorption Spectra and Calculated Results for Aryl *p*-Benzoquinones



1



2

	X	*R*	*Observed*[a]		*Calcd*[b]	
			λ_{max} *(nm)*	ε	λ_{1max} *(nm)*	f_1
1a	H	Me	561	5960	561	0·3080
1b	H	Et	581	6600	581	0·3203
1c	5-OMe	Me	558	6560	543	0·3193
1d	5-F	Me	581	6180	553[c]	0·3170
1e	5-Cl	Me	598	6120	557[c]	0·3122
1f	6-Cl	Me	595	5090	559[c]	0·3014
1g	3,5-Cl_2	Me	615	3890	563[c]	0·2979
1h	3,6-Cl_2	Me	608	3190	565[c]	0·2872
2a	H	Me	559	3930	561	0·3127
2b	5-OMe	Me	557	4800	543	0·3247
2c	5-F	Me	581	4830	554[c]	0·3217
2d	5-Cl	Me	600	4600	557[c]	0·3169
2e	3-COMe	Me	584	3260	596	0·4032
2f	3-COOMe	Me	590	3190	604	0·3904
2g	3-CN	Me	640	5440	600[c]	0·4392
2h	3,5-Cl_2	Me	626	2530	576[c]	0·2869
2i	3,6-Cl_2	Me	609	2160	579[c]	0·2764

[a] Measured in EtOH.
[b] VSIP of N, 24·50 (NMe_2), 23·90 (NEt_2).
[c] New parameters indicated in Table 1 were used.

TABLE 3
Steric Effects on the First Excitation Energy of **2a**

Twist angle (degree)	*Bond (a)*		*Bond (b)*	
	ΔE_1 *(eV)*	f_1	ΔE_1 *(eV)*	f_1
10	2·153	0·3244	2·159	0·3290
20	2·144	0·3074	2·168	0·3262
25	2·135	0·2939	2·175	0·3243
30	2·123	0·2762	2·182	0·3220
35	2·107	0·2552	2·190	0·3192
40	2·087	0·2305	2·197	0·3158

incorporated with the steric effects, and the twist angle was estimated to be 35 degrees from comparison of the observed λ_{max} values with the calculated values (λ_1).

3 RESULTS AND DISCUSSION

3.1 Comparison of the observed absorption maximum (λ_{max}) with the calculated value (λ_1)

The observed λ_{max} values and the calculated results are shown in Table 2. In general, a good linear correlation between the observed values and the calculated results for the first excitation was found, except for halogeno and cyano derivatives. However, correlations between the oscillator strength (f_1) obtained by calculation and the molar extinction coefficient (ε) obtained from experimental data are unsatisfactory in many cases, because of the difficulty in reflecting the steric hindrance in the MO calculations.

Dye **1** showed a large positive solvatochromism, as shown in Table 4. As indicated, dye **1** has a strong intramolecular charge-transfer (CT) chromophoric character and produced a large bathochromic shift of λ_{max} from nonpolar solvents to polar or protic solvents. Introduction of a halogeno group (**1d**, **1e**) into the benzoquinone moiety strengthens the CT character and $\Delta\lambda$ then increased much more than that of the unsubstituted dye (**1a**).

The observed λ_{max} values of the halogeno substituted dyes have not been appreciably reproduced in the PPP MO method because the electronic effects of halogen atoms mainly operate through the sigma framework (negative inductive effect).

TABLE 4
Effect of Solvents on the λ_{max} of *p*-Benzoquinones

Compd	*Calcd*	*Observed*				
		C_6H_{12}	*EtOH*		*DMSO*	
	λ_1[a] *(nm)*	λ_{max} *(nm)*	λ_{max} *(nm)*	$\Delta\lambda$[b]	λ_{max} *(nm)*	$\Delta\lambda$[b]
1a	529	528	561	(33)	565	(37)
1b	548	547	581	(34)	585	(38)
1c	515	513	558	(45)	559	(46)
1d	523	539	581	(42)	588	(49)
1e	526	556	598	(42)	596	(40)

[a] VSIP of N; 25·50 eV (NMe_2), 24·90 eV (NEt_2).
[b] Difference in λ_{max} between observed values in C_6H_{12} and those in each solvent.

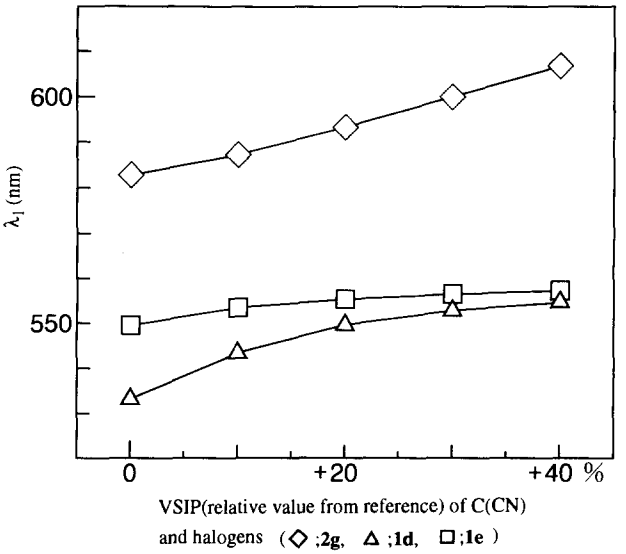
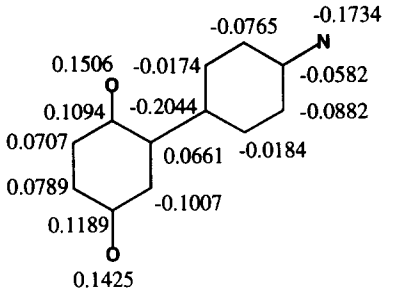


Fig. 4. Relationship between λ_1 on VSIP(eV) of C(CN) and halogens.

The dependence of ΔE_1 on the VSIP of the halogen atoms was examined by using **1d** and **1e** as examples, and the results are shown in Fig. 4. The calculations were carried out using the parameters given in Ref. 14. It was found that the ΔE_1 values of the halogeno dyes are virtually unaffected (at most 10 nm) by the VSIP value of halogen atom.

The large bathochromic shift of the halogeno substituted dyes (**1d–1f**) in comparison with the corresponding calculated λ_1 was attributed to parameterization of the halogen atoms. From our estimations, E_A values of halogen atoms should be increased much more, in order to evaluate the strong electron-withdrawing effect of these atoms in the quinone ring. Dye **1a** has a strong intramolecular CT chromophoric system, and the push-pull effect directly produce a large bathochromic shift. Comparison of the electron-donating properties of the amino group in the chromophore systems of 4-aminoazobenzene (I), 1-aminoanthraquinone (II) and 2-(4-aminophenyl)-*p*-benzoquinone (III) were evaluated by the slope of the linear relationship when the ΔE_1 values were plotted against the VSIP values of the amino group. The values of the slope were in the order of III (0·120) > II (0·107) > I (0·084). These results indicated that III has the strongest intramolecular charge-transfer chromophoric system of the three components.

The cyano derivative (**2g**) produced a large bathochromic shift of over 80 nm compared with **2a**, and the calculated λ_1 did not replicate the observed value (Table 2). The parameters of the cyano group have been reported by Griffiths[15] and Kogo,[4] as indicated in Table 1, but the use of these values could not reproduce the observed value of dye **2g**.



1a

Fig. 5. π-Electron density changes accompanying the first excitation.

The π-electron density changes accompanying the first excitation of **1a** were calculated and the results are shown in Fig. 5. Decrease of electron density at the 3-position, and increase of those at 5- and 6-positions, were observed. These tendencies have been previously reported in *p*-benzoquinone chromophore[2] and in aryl 1,4-naphthoquinones.[13] However, the 3-cyano group, as a strong acceptor in **2g**, produced a large bathochromic shift of λ_{max}. From our simulations, the VSIP value of the carbon atom in the cyano group should be increased at least 30% to reproduce the λ_{max} value, and a new parameterization for the cyano group was carried out as indicated in Table 1. These modification of parameters are proposed to be reasonable for the case of strong push-pull chromophores such as dye **1**.

3.2 Steric effect evaluated by ^{1}H NMR spectra

Steric effects in dye **2** cause differences in the chemical shifts ($\Delta\delta$) of the aryl ring protons in comparison with those of dye **1**. The NMR data of the aromatic protons are summarized in Table 5. The $\Delta\delta$ values indicate the effects of steric hindrance in each pair of dyes. Higher-field shifts of all protons in the aryl ring were generally observed. The positive mesomeric effect of the 2'-methoxy group caused a higher-field shift at 3'-H and 5'-H. However, steric hindrance in dye **2** reduced the conjugation between the aryl and quinone moieties also causing a higher-field shift of all the aryl protons.

In conclusion, the largest $\Delta\delta$ values were observed for 3'-H, but 5'-H and 6'-H were also shifted to higher-field by 0·3–0·4 ppm. On the other hand, the strong electron-withdrawing effect of the 3-cyano group in dye **2g** produced a large lower-field shift of 6'-H (0·15 ppm) in spite of the steric hindrance between the 3-substituent and an aryl ring. In contrast, the 3-acetyl substituted dye (**2e**) produced a higher-field shift of 6'-H (0·19 ppm), which might be caused by the steric effect being stronger than its electron-

TABLE 5
^{1}H NMR Data of Aromatic Protons (δ, ppm)

Compound	*3'-H*	$\Delta\delta$	*5'-H*	$\Delta\delta$	*6'-H*	$\Delta\delta$
1a	6·74		6·74		7·50	
2a	6·22	0·52	6·34	0·40	7·08	0·42
1c	6·74		6·74		7·50	
2b	6·21	0·53	6·33	0·41	7·12	0·38
1e	6·72		6·72		7·50	
2d	6·23	0·49	6·35	0·37	7·14	0·36
1g	6·74		6·74		7·31	
2h	6·22	0·52	6·36	0·38	7·03	0·28
1h	6·74		6·74		7·31	
2i	6·24	0·50	6·38	0·36	7·04	0·27
2a	6·22	—	6·34	—	7·08	—
2e	6·19	0·03	6·29	0·05	6·89	0·19
2f	6·19	0·03	6·29	0·05	7·00	0·08
2g	6·20	0·02	6·38	−0·04	7·23	−0·15

withdrawing effect. These NMR results thus satisfactorily explain the substituent effects in the absorption spectra in dyes **2**.

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