Semi-empirical MO-calculations on the electronic spectra of azido substituted *p*-benzoquinones*

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Abstract—The electronic spectra of azido substituted *p*-benzoquinone (PBQ) have been recorded. The energy levels have also been calculated by means of PPP–CI method and on the basis of this assignments are made for the observed absorption bands. The results show that the Tetraazido *p*-benzoquinone has an $n-\pi^*$ transition at 570 nm and three allowed $\pi-\pi^*$ transitions at 380, 278 and 215 nm. The 2,5-diazido-3,6-dichloro *p*-benzoquinone has an $n-\pi^*$ transition at 430 nm and two allowed $\pi-\pi^*$ transitions at 335 and 210 nm. Replacement of the chlorine atoms by $-OCH_3$ and $-NH_2$ groups does not alter the spectra appreciably. Inversion of symmetry is shown to result in an allowed transition from HOMO to LVMO in chloranil whereas it is forbidden in the case of azidanil. A comparison of the E_{HOMO} and E_{LVMO} with those of chloranil suggests that the azido substituted quinones are also efficient electron acceptors.

INTRODUCTION

We have determined the electronic spectra of substituted azido *p*-benzoquinones. The electronic spectra of PBQs show characteristic behaviour depending on the properties of the substituents. STEVENSON [1] has studied theoretically the spectra of some substituted PBQs using the perturbation approach. However, no work has been done on the electronic spectra of azido substituted PBQs. In this paper the electronic spectra for such compounds have been calculated by means of PPP-CI method and on the basis of this assignments are made for the observed absorption bands.

EXPERIMENTAL

Materials

(a) Azidanil. It was prepared by a slight modification of FRIES' method [2]. Chloranil (4.59 g) suspended in 80 cm³ of ethanol was mixed with Sodium azide (5.86 g) and shaken for 8 h. in a horizontally rotating shaker. Then the mixture was poured into water to precipitate the solid azidanil in near quantitative yield. The crystals were filtered and dried in vacuum. It was then recrystallised thrice from ethanol.

(b) 2,5-diazido-3,6-dichloro-1,4-benzoquinone (DADCQ). The method was essentially that proposed by FRIES [2]. Chloranil (4.59 g) was suspended in 100 cm³ of acetone and sodium azide (2.95 g) in 5 cm³ of water was added slowly with constant shaking. The DADCQ separated out as orange red crystals. This was then filtered and washed with acetone and water and recrystallised from benzene twice.

(c) 2,5-diazido-3,6-dimethoxy-1,4-benzoquinone (DADMQ).

It was prepared from 2.5-dichloro-3,6-dimethoxy *p*-benzoquinone [3] following the procedure adopted by WINKEL-MANN [4]. The dichloro dimethoxy benzoquinone (2.37 g) was suspended in 20 cm³ of methanol and sodium azide (1.43 g) was added in portion with constant shaking. The reaction mixture was then cooled, filtered and then washed with water and ice-cold methanol. It was then recrystallised twice from methanol.

(d) 2,5-diazido-3,6-diamino-1,4-benzoquinone (DADAQ). 2,5-Dichloro-3,6-Diamino p-benzoquinone [5] (2.16 g) was suspended in 15 cm³ of methanol and Sodium azide (1.35 g) was added with constant shaking. The temperature of the mixture was kept constant at 20° C. The brownish black quinone separated was filtered and washed with water, ether and finally with ice-cold methanol. The quinone was then recrystallised from the methanol-water mixture.

All crystalline products were tested for purity from constance of ε_{max} .

Measurements

All the solvents used were of spectral grade. The u.v. absorption spectra at room temperature were determined in 1 cm cells using a Hilger-Watts u.v. Spectrophotometer. The accuracy of λ_{max} is about ± 2 nm and the precision of ε_{max} values is better than 5%.

Table 1 summarised the experimental results on the absorption bands for the studied compounds. The spectra of DADAQ, DADCQ and DADMQ could not be measured in hexane and cyclohexane because of their insolubility in the above solvents. The experimental oscillator strengths (f) values were calculated from the formula [6]

$$f = 4.32 \times 10^{-9} \times \varepsilon_{\text{max}} \times 1.06 \times h$$

where h is the half band width in cm^{-1} and ε is the molar extinction coefficients in M^{-1} cm⁻¹ or by the approximate one [7]

$$f = 2 \times 10^{-5} \times \varepsilon_{\text{max}}$$
 for shoulders

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Compound	Solvent	$\lambda_{\max}(nm)$	log ε
Azidanil	С	570	2.39
		382	4.14
		281	4.41
		210	4.18
	MC	550	2.48
		368	4.12
		275	4.40
		215	4.43
	н	570	2.42
		380	4.26
		278	4.55
		215	4.26
	М	540	2.50
		355	4.11
		268	4.41
		205	4.47
Diazido dichloro	MC	430	2.98
p-benzoquinone		338	4.30
		262	4.29
		213	4.07
Diazido diamino	М	520	2.52
p-benzoquinone		337	4.44
		245	4.01
		215	4.29
Diazido dimethoxy	М	485	2.49
p-benzoquinone		332	4.11
		263	4.15
		210	4.16

C is cyclohexane, H is n-hexane, MC is methyl cyanide, M is methanol.

METHOD OF CALCULATION

The semi-empirical PPP-CI calculations were performed for the π -electronic singlet spectra. It is assumed



Fig. 1. The solution spectra of (a) tetraazido *p*-benzoquinone in cyclohexane; (b) Dichloro diazido *p*-benzoquinone in methyl cyanide. that the molecules studied have a planar structure and that the quinone ring consists of regular hexagons with every bond length equal to 1.40 Å. The other bond lengths for azidanil are given below.



The resonance integral β_{rs}^{core} was calculated using the Ohno's formula [8]

$$\beta_{rs}^{\text{core}} = \frac{1}{2}(N_r + N_s)S_{rs}(\gamma_{rs} - 28.79 \ c/d_{rs})$$

where N, represent the number of π -electrons donated to the conjugated systems by atom r, d_{rs} is the r—s bond distance,

$$\gamma_{rs} = \frac{14.395}{(d_{rs}^2 + b^2)^{1/2}}; b = \frac{28.79}{(\gamma_{rr} + \gamma_{ss})}$$

and c is the Ohno's constant assumed to be 0.85. It is assumed that the central nitrogen of the azido group donates two electrons to the π -system. The calculated resonance integrals are given in Table 2. The coloumb repulsion integrals are obtained by Mataga method [9]. Sixteen singly excited configurations are included in the CI calculations of all molecules.



Fig. 2. The solution spectra of (a) diamino diazido *p*-benzoquinone in methanol; (b) Dimethoxy diazido *p*-benzoquinone in methanol.

Table 2. The values of resonance integrals

Bond	Length Å	β_{rs}^{core} (eV)
с-с	1.40	-2.4235
C - N(1)	1.47	-1.5220
C - N(2)	1.47	1.8693
CO(1)	1.14	- 3.0697
C - Cl(2)	1.43	-2.1177
N(1) - N(2)	1.24	-2.9857
N(1) - N(2)	1.13	-4.2907













(e)

Fig. 3. The charge density distribution of substituted p-benzoquinones. (a) Azidanil; (b) Diazido dichloro pbenzoquinone; (c) Diazido dimethoxy p-benzoquinone; (d) Diazido diamino p-benzoquinone; (e) Chloranil.

RESULTS AND DISCUSSION

The calculated energies and oscillator strength (f) for lower excited states of the various azido substituted PBQs are presented in Table 3 together with the observed data. The electronic states are classified according to the symmetry of the molecule.

(a) Azidanil (D_{2h})

It is observed that the molecule has four absorption bands at 2.17 eV (570 nm), 3.24 eV (380 nm), 4.41 eV (278 nm) and 5.82 eV (215 nm) respectively. The electronic configuration for the four highest occupied orbitals is $a_x^2 b_{3g}^2 b_{1w}^2 b_{2g}^2$. The solution spectrum in various solvents is shown in Table 1. The band near 2.17 eV (570 nm) shows solvent shift characteristic [10] of transition involving non-bonded electrons. This evidence coupled with the improbability of a $\pi \rightarrow \pi^*$ transitions in this range leads to the possible assignment of the band to a $n-\pi^*$ transition.

The highly intense band at 3.24 eV (380 nm) could be assigned to the $\pi \rightarrow \pi^*$ transition involving the state ${}^{1}B_{2u}$ arising from the orbital transition $b_{3g} \leftarrow b_{1u}$. There

(c)

Table 3. Excited states of azido p-benzoquinones

Energy (eV)		rgy (eV)	Oscillator strength			
State (Symmetry)(Calculated	Observed	Calculated	Observed		
Azidanil (Đ _{2k})						
$\psi_1(B_{1g})$	2.50		0.00			
$\psi_2(B_{2\mu})$	3.34	3.25	0.80	0.19		
$\psi_3(B_{2u})$	4.12	4.41	0.08	0.66		
$\psi_{\mathbf{A}}(B_{3w})$ $\psi_{\mathbf{A}}(B_{2w})$	4.69		1.94 (
$\psi_6(B_{3\mu})$	6.05	5.82	1.47	0.17		
	Triazido m	onochloro p	-benzoquinor	ne		
ψ1	2.58		0.05			
ψ_2	3.47		0.65			
¥3	4.63		0.90			
ψ_4	4.81		0.11			
Ψ5	4.94		0.49			
Ψ6	5.25		0.08			
Ψ_7	5.50		0.08			
Ψ8	5.91		0.02			
Ψ9 Ψ10	6.08		1.34			
ſ	Diazido dici	hloro <i>p</i> -benz	zoquinone (C ₂	2 h)		
$\psi_1(A_q)$	2.72		0.00			
$\psi_2(B_u)$	3.45	3.67	0.68	0.32		
$\psi_3(B_u)$	4.66	4.73	0.48	0.50		
$\psi_4(B_u) \\ \psi_5(B_u)$	4.86 5.70	5.82	0.85	0.17		
	Monoazido trichloro a-benzoquinone					
	288	· · · ·	0.12			
Ψ_1	4 22		0.72			
¥2 ¥2	4.89		0.56			
Ý.	5.92		0.03			
¥ 5	6.08		0.39			
Ψ6	6.67		0.27			
Chloranil (D _{2k})						
$\psi_1(B_{1s})$	3.26		0.00			
$\psi_2(B_{2u})$	4.39	4.32	0.83	0.20		
$\psi_{3}(\boldsymbol{B}_{1g})$	6.14		0.00			
Diazido diamino <i>p</i> -benzoquinone (C_{2h})						
$\psi_1(A_g)$	2.42	3 69	0.00	0.26		
$\Psi_2(B_w)$	3.40 4 37)	3.08	0.62	0.30		
$\psi_3(D_\mu)$	4.50	4.97	0.24	0.24		
$\psi_4(D_u)$	5 44		0.221			
$\psi_6(B_u)$	6.09	5.82	0.40	0.61		
Diazido dimethoxy <i>p</i> -benzoquinone (C_{2h})						
$\psi_1(A_g)$	2.29		0.00			
$\psi_2(B_u)$	3.36	3.73	0.59	0.25		
$\psi_3(B_u)$	4.17	4.73	0.78	0.38		
$\psi_4(B_n)$	4.53		0.21			
$\psi_5(B_u)$ $\psi_6(B_u)$	5.29 5.99	5.82	0.20	0.26		

are two allowed transitions at 4.12 and 4.69 eV arising from the transitions to the states ${}^{1}B_{2u}$ $(b_{3g} \leftarrow b_{1u})$ and ${}^{1}B_{3u}$ $(b_{1u} \leftarrow b_{2g})$ respectively and the absorption at 4.40 eV (278 nm) could be identified to these. The band at 5.80 eV (215 nm) is due to the two allowed transitions to the states ${}^{1}B_{2u}$ and ${}^{1}B_{3u}$.

(b) DADCQ, DADMQ and DADAQ (C_{2h})

All these iso π -electronic molecules have nearly similar spectra. The DADCQ has a shoulder at 2.88 eV (430 nm) and could be assigned to an $n \rightarrow \pi^*$ transition. The replacement of the chlorine by $-\text{OCH}_3$ and $-\text{NH}_2$ groups shifts this shoulder to 2.55 eV (485 nm) and 2.38 eV (520 nm) respectively. The band around 3.60 eV (335 nm) of these molecule arise from $\pi \rightarrow \pi^*$ transition to the state ¹B_u (around 3.40 eV). The two allowed transitions at 4.66 and 4.86 eV give rise to the band at 4.73 eV (262 nm). In the case of DADAQ this band appears as a shoulder at 5.06 eV (245 nm). The band at 5.82 eV (210 nm) is due to the allowed transition to the state of energy 5.70 eV. In the case of DADAQ and DADMQ the band around 5.82 eV (210 nm) is due to two allowed transitions.

However the calculated results reveal that the parameters chosen for $-OCH_3$ and $-NH_2$ groups are not very good in predicting the experimental results.

The calculation shows that the electronic configuration of chloranil is $b_{1u}^2 b_{2g}^2 b_{3g}^2 a_u^2 b_{1u}^2 b_{3g}^2 b_{2g}^2 b_{1u}^2$. It is interesting to note that there is an inversion of symmetry of the two highest occupied MOs compared to that of azidanil. Hence the transition from HOMO to the LVMO is an allowed one in chloranil whereas that in azidanil is forbidden.

Although the triazido monochloro and Monoazido trichloro PBQs could not be isolated because of instability their spectra have been calculated for comparison. On replacing the chlorine atoms by azido groups the energy levels of the corresponding excited states shifts towards the lower values. However a comparison of the charge distributions show that the

Molecule	Energy of HOMO (eV)	Energy of LVMO (eV)	Electron affinity* (eV)
Chloranıl	- 10.79	-4.00	2.10 (2.46)†
Azıdanıl	-9.11	- 3.58	1.68
Triazido monochloro	-9.23	- 3.63	1.73
benzoquinone			
Diazido dichloro	-9.62	- 3.68	1.78
benzoquinone			
Monoazido trichloro	-9.77	-3.83	1.93
benzoquinone			
Diazido dimethoxy	-8.96	- 3.39	1.49
benzoquinone			
Diazido diamino	-9.19	- 3.49	1.59
benzoquinone			

*Calculated by the relation of KUNII and KURODA, reference [13].

†Experimental value, Reference [14].

electron density on the quinone ring is not appreciably altered by the substituents studied here. Also the energies of HOMO and LVMO (Table 4) suggests that the azido quinones are efficient electron acceptors almost equal to chloranil. It may be noted that in the case of DADCQ the electron affinity values obtained by CT measurements [11, 12] has been found to be very close to that of chloranil.

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