

Spectral properties of some amino substituted *p*-benzoquinones

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MS received 5 February 1979

Abstract. Electronic spectra of amino substituted *p*-benzoquinones (PBQ) have been recorded and the bands assigned on the basis of PPP-CI calculations. The results show that the aminoquinones have two allowed π - π^* transitions around 3.70 eV and 5.65 eV. The n - π^* transition of tetra-amino *p*-benzoquinone is found to be almost ten times more intense than that of diamino *p*-benzoquinones. A comparison of methoxy and amino *p*-benzoquinones gives strong evidence for the quinonoid character for the latter rather than a quadrupolar merocyanine structure. An examination of the infrared spectra suggests the existence of intramolecular hydrogen bonding in aminoquinones.

Keywords. Electronic spectra; infrared spectra; aminoquinones; methoxy quinones.

1. Introduction

The biological importance of *p*-benzoquinone and its derivatives (Cooper 1913, 1927; Kway-Yuen Zee-Cheng and Cheng 1970; Khan and Driscoll 1976; Wallenfels and Draber 1964) has been responsible for the considerable interest in the chemistry of these compounds. Study of the structural and biochemical properties of 2,5-diamino *p*-benzoquinones is interesting because of their potential applications in oncology. Leupold and Dahne (1965) and Kulpe *et al* (1966) have indicated by x-ray structure determination that amino substituted *p*-benzoquinones exist only as quadrupolar merocyanins. Klessinger (1966), on the other hand, favours the quinone structure. Since no systematic studies have been made on the electronic and the infrared spectra of compounds such as 2,5-diamino-3,6-dichloro *p*-benzoquinone (DADCQ) and 2,3,5,6-tetra-amino *p*-benzoquinone (TABQ), we report here the electronic spectra of the above compounds and compare them with the results from semi-empirical theoretical calculation. We also report the spectra of 2,3,5,6-tetramethoxy *p*-benzoquinone (TMBQ) and 2,5-dichloro-3,6-dimethoxy *p*-benzoquinone (DCDMQ) for comparison.

2. Experimental

2.1. 2,5-Diamino-3,6-dichloro *p*-benzoquinone (DADCQ)

It is prepared by the method of Fieser and Martin (1935), by passing dry ammonia into a suspension of chloranil in hot alcohol.

2.2. 2,3,5,6-tetra-amino *p*-benzoquinone (TABQ)

The method is essentially due to Winkelmann (1969). It is prepared by hydrolysing 2,5-bis(acetylamino)-3,6-diamino-*p*-benzoquinone(I) with conc. H_2SO_4 . A mixture of I and 75 ml of conc. H_2SO_4 are taken in a round-bottomed flask and is stirred at a temperature of 70 to 80° C for 2 hr. It is then cooled and the reaction mixture is poured into ice cold water to get TABQ. $2H_2SO_4$. It is filtered and the TABQ is obtained by treating TABQ sulfate with 10% $NaHCO_3$ solution. It is further purified by reduction into the corresponding quinol and reoxidation with $FeCl_3$.

2.3. 2,5-Diamino-3,6-dimethoxy *p*-benzoquinone (DADMQ)

It is prepared by the method of Neeh and Bayer (1957). The 2,3,5,6-tetra-methoxy *p*-benzoquinone is taken in 250 ml of boiling alcohol and dry ammonia gas is passed through the solution for 10 hr. A dark coloured substance is obtained when cooled. It is then washed with water, alcohol and ether and then recrystallised from absolute alcohol.

2,5-Dichloro-3,6-dimethoxy *p*-benzoquinone (DCDMQ) and 2,3,5,6-tetra-methoxy *p*-benzoquinone (TMBQ) are prepared by the method of Vertor and Rogers (1966). All the products were tested for purity from the constancy of ϵ_{max} .

3. Measurements and calculation

All the solvents used were of spectral grade. The ultraviolet absorption spectra are measured using Hilger Watts UV spectrophotometer. The infrared spectra are recorded using Perkin-Elmer Grating infrared spectrophotometer (Model No. 577) in KBr solid.

The semi-empirical PPP-CI calculations are essentially the same as in our previous communication (Chandra Singh *et al* 1979).

4. Results and discussion

Electronic spectra of the various quinones studied are shown in figures 1 and 2 and positions of absorption maxima are listed in table 1. Calculated spectra of the various compounds along with the observed values are given in table 2; the electronic energy states are classified in terms of the symmetry group of the molecule.

From an examination of figure 1, wherein the spectra of the diamino substituted quinones are given along with that of DCDMQ, it is clear that the electronic

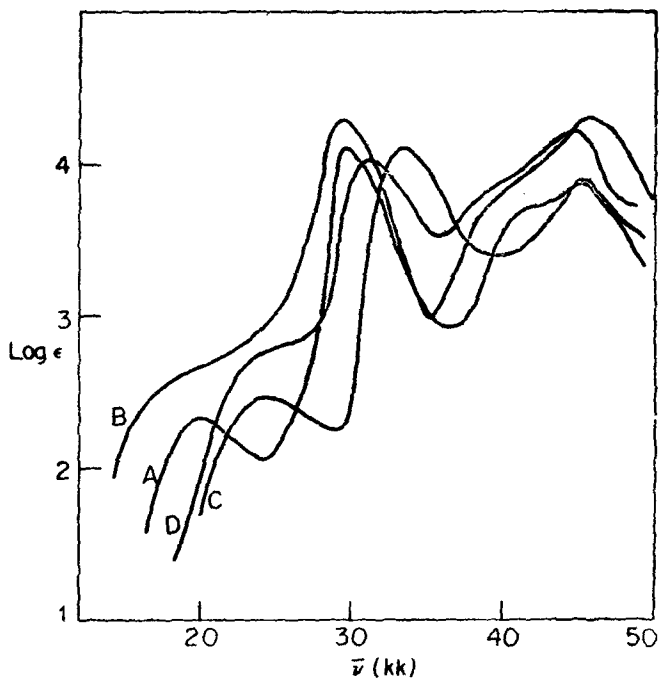


Figure 1. Electronic spectra of substituted quinones.
 (A) Diamino dichloro *p*-benzoquinone; (B) Diamino dimethoxy *p*-benzoquinone;
 (C) Dichloro dimethoxy *p*-benzoquinone; (D) Bis(acetylamino) dichloro *p*-benzoquinone.

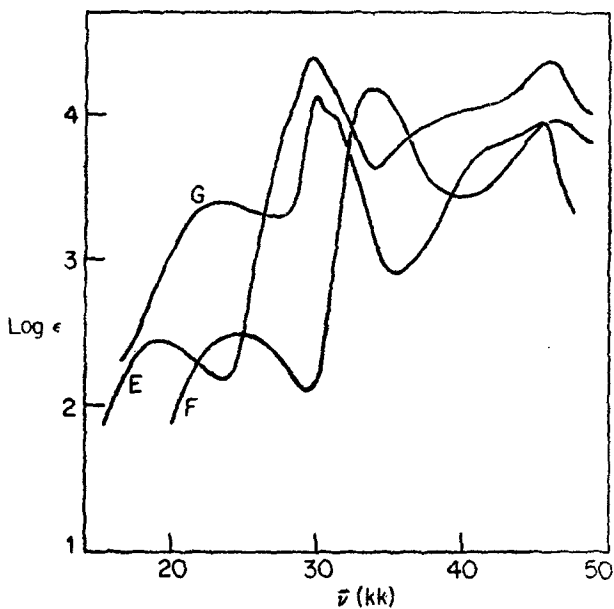


Figure 2. Electronic spectra of substituted quinones.
 (E) Bis(acetylamino) diamino *p*-benzoquinone; (F) Tetramethoxy *p*-benzoquinone;
 (G) Tetraamino *p*-benzoquinone.

Table 1. Absorption spectra of amino substituted *p*-benzoquinones.

Compound	Solvent	λ_{\max}	log ϵ
2,3,5,6-Tetra-amino <i>p</i> -benzoquinone	Acetonitrile	440	3.40
		337	4.14
		240 (sh)	3.77
		218	3.97
2,5-Diamino-3,6-dichloro <i>p</i> -benzoquinone	Dioxane	500	2.32
		335	4.11
		240 (sh)	3.71
		220	3.88
2,5-Diamino-3,6-dimethoxy <i>p</i> -benzoquinone	Methanol	560	2.57
		342	4.33
		242 (sh)	3.91
		220	4.31
2,3,5,6-Tetramethoxy <i>p</i> -benzoquinone	Cyclohexane	403	2.48
		295	4.20
		215	3.97
2,5-Dichloro-3,6-dimethoxy <i>p</i> -benzoquinone	Cyclohexane	406	2.48
		300	4.11
		216	3.90
2,5- <i>bis</i> (acetylamino)- 3,6-dichloro <i>p</i> -benzoquinone (DAcDCQ)	Acetonitrile	410	2.77
		320	4.05
		255 (sh)	3.84
		221	4.20
2,5- <i>bis</i> (acetylamino)- 3,6-diamino <i>p</i> -benzo- quinone (DAcDAQ)	Dioxane	520	2.45
		340	4.38
		255 (sh)	4.00
		215	4.36

(sh) = shoulder.

spectra of all these compounds are very similar. Hence it can be understood that the quinonoid character is very strong and dominating in the aminoquinones. All the three compounds DADCQ, DADMQ and DCDMQ possess a forbidden low lying $\pi-\pi^*$ state with a symmetry 1A_g resulting from the transition from the HOMO to the LVMOs ($b_g \leftarrow b_g$). The compounds DADCQ and DADMQ possess an $n-\pi^*$ transition around 2.5 eV, whereas DCDMQ shows at ~ 3.0 eV. There is an allowed $\pi-\pi^*$ transition having the symmetry 1B_u around 3.7 eV (335nm) (table 1) for the three diaminoquinones due to the orbital transition ($b_g \leftarrow a_u$). In the case of DCDMQ, this band shifts to the higher energy (4.14 eV). The band around 5.6 eV in the diamino quinones is due to the allowed $\pi-\pi^*$ transition due to the orbital transition ($b_g \leftarrow a_u$) resulting in the state of symmetry 1B_u . However in DCDMQ, calculations show the inverted transition ($a_u \leftarrow b_g$) for this band leading to the same symmetry.

Table 2. Excited states of amino substituted *p*-benzoquinone.

State (symmetry)	Energy (eV)		Oscillator strength	
	Calc.	Observed	Calc.	Observed
<i>Tetra-amino p</i> -benzoquinone (D_{2h})				
$\psi_1 (B_{1g})$	2.31		0.00	
$\psi_2 (B_{2u})$	3.71	3.68	0.64	0.16
$\psi_3 (B_{1g})$	5.81		0.00	
		5.18 (sh)		0.12
$\psi_4 (B_{2u})$	5.85	5.65	0.20	0.16
$\psi_5 (A_g)$	5.93		0.00	
<i>Diamino dichloro p</i> -benzoquinone (C_{2h})				
$\psi_1 (A_g)$	2.79		0.00	
$\psi_2 (B_u)$	4.02	3.71	0.73	0.15
$\psi_3 (A_g)$	5.95		0.00	
		5.18 (sh)		0.10
$\psi_4 (B_u)$	5.98	5.65	0.12	0.20
<i>Diamino dimethoxy p</i> -benzoquinone (C_{2h})				
$\psi_1 (A_g)$	2.21		0.00	
$\psi_2 (B_u)$	3.59	3.65	0.64	0.31
$\psi_3 (A_g)$	5.72		0.00	
		5.13 (sh)		0.16
$\psi_4 (B_u)$	5.74	5.64	0.27	0.59
$\psi_5 (A)$	5.82		0.00	
<i>Tetramethoxy p</i> -benzoquinone (D_{2h})				
$\psi_1 (B_{1g})$	2.04		0.00	
$\psi_2 (B_{2u})$	3.47	4.20	0.64	0.36
$\psi_3 (B_{1g})$	5.63		0.00	
$\psi_4 (A_g)$	5.68		0.00	
$\psi_5 (B_{3u})$	5.75		0.01	
$\psi_6 (B_{2u})$	5.89	5.77	1.26	0.26
$\psi_7 (B_{3u})$	6.01		0.58	
<i>Dichloro dimethoxy p</i> -benzoquinone (C_{2h})				
$\psi_1 (A_g)$	2.63		0.00	
$\psi_2 (B_u)$	3.86	4.14	0.70	0.33
$\psi_3 (B_u)$	5.86	5.75	0.18	0.20
$\psi_4 (A_g)$	5.87		0.00	

As in diaminoquinones, the spectra of TABQ, DAcDAQ and TMBQ are close to each other (figure 2). All these compounds show an $n-\pi^*$ transition around 2.7 eV. However the $n-\pi^*$ transition of TABQ is almost ten times

stronger than that of DAcDAQ and TMBQ. Both TMBQ and TABQ have low lying forbidden $\pi-\pi^*$ state (${}^1B_{1g}$) due to the transition $b_{2g} \leftarrow b_{2g}$. There is an allowed $\pi-\pi^*$ transition at 3.7 eV having the symmetry ${}^1B_{2u}$ resulting from the orbital transition $b_{3g} \leftarrow b_{1u}$. The band around 5.65 eV is due to the $\pi-\pi^*$ transition (${}^1B_{2u}$) due to the orbital transition $a_u \leftarrow b_{2g}$. The calculation shows that there is a cluster of energy levels in this region. Thus the closeness of the spectra of TABQ, DAcDAQ with that of TMBQ and the close agreement between the experiments

Table 3. Infrared absorption spectra in the region of 1400 cm^{-1} to 4000 cm^{-1} .

Compound	4000–2000 cm^{-1} region	2000–1400 cm^{-1} region
2,3,5,6-Tetra-amino <i>p</i> -benzoquinone	3382 (b; s.) 3320 (b; s.) 3238 (b; s.) 3182 (b; s.)	1578 (b; s.)
2,5-Diamino-3,6-dichloro <i>p</i> -benzoquinone	3384 (s; s.) 3345 (s; w.) 3230 (b; s.) 3172 (b; s.)	1670 (s; w.) 1622 (sh; m.) 1571 (b; s.)
2,5-Diamino-3,6-dimethoxy <i>p</i> -benzoquinone	3400 (s; s.) 3311 (b; s.)	1659 (s; s.) 1548 (b; s.) 1439 (s; m.)
2,5-Bis (acetylamino)-3,6-diamino <i>p</i> -benzoquinone	3347 (b; s.) 3190 (b; s.)	1642 (s; s.) 1564 (b; s.) 1495 (s; s.)
2,5-Bis (acetylamino)-3,6-dichloro <i>p</i> -benzoquinone	3258 (s; s.) 3192 (sh; m.) 2980 (s; w.)	1696 (s; s.) 1669 (s; s.) 1611 (s; m.) 1502 (s; s.)
2,5-Dichloro-3,6-dimethoxy <i>p</i> -benzoquinone	3036 (s; v.w.) 2968 (s; v.w.) 2862 (s; v.w.)	1683 (s; s.) 1660 (s; s.) 1628 (s; s.) 1573 (s; s.) 1450 (s; m.)
2,3,5,6-Tetramethoxy <i>p</i> -benzoquinone	3020 (s; v.w.) 2964 (s; v.w.) 2945 (s; v.w.) 2840 (s; v.w.)	1665 (s; m.) 1604 (s; s.) 1476 (s; w.) 1460 (s; w.) 1438 (s; w.)

sh—shoulder;

b.—broad;

s.—sharp;

v.w.—very weak,

s.—strong

m.—medium

w.—weak

and the calculations clearly suggest a strong quinonoid character for these tetra-amino substituted quinones.

One characteristic feature to be noted in the spectra of aminoquinones, which is absent in TMBQ and DCDMQ, is that both the allowed $\pi-\pi^*$ transitions bands exhibit well-defined shoulders which may be ascribed to intramolecular hydrogen bonding (Herzberg 1966; Kulpe 1971).

In order to strengthen our argument based on the electronic spectra, we have taken the infrared spectra of the above compounds and the results are summarised in table 3. An examination of the spectra reveals a broad peak around 3250 cm^{-1} , characteristic of hydrogen bonded systems. Further in the case of DAcDCQ, the peak at 1610 cm^{-1} characteristic of the ring $\text{C}=\text{O}$ stretching of the quinone, is very sharp but that of DADCQ, DAcDAQ and TABQ are intense and shallow and shifts to lower energy. These highly intense and broad peaks cannot be assigned as due to the $\text{C}=\text{C}$ and $\text{C}=\text{N}$, since the intensities of these modes are usually not intense in the infrared. Hence these bands must be assigned as due to $\text{C}=\text{O}$. Similar observations have been made by several workers in other systems such as acetylacetone, dibenzoyl methane (Rasmussen *et al* 1949a, b Honsberger *et al* 1952) and D-lupanine N-oxide perchlorate (Baranowski *et al* 1964). These authors ascribed these intense and broad peaks to the intra and intermolecular hydrogen bondings. Hence it may be concluded that the same should also be operative in aminoquinones. However, we are not able to differentiate here between intra and intermolecular hydrogen bonding since the infrared spectra were taken in solid state; insolubility of these aminoquinones in most of the solvents makes the solution study difficult.

Further it may be noted that the π -electron charge densities of these molecules given in figure 3 show that the charge distributions are not much disturbed in aminoquinones compared to that of the methoxy quinones.

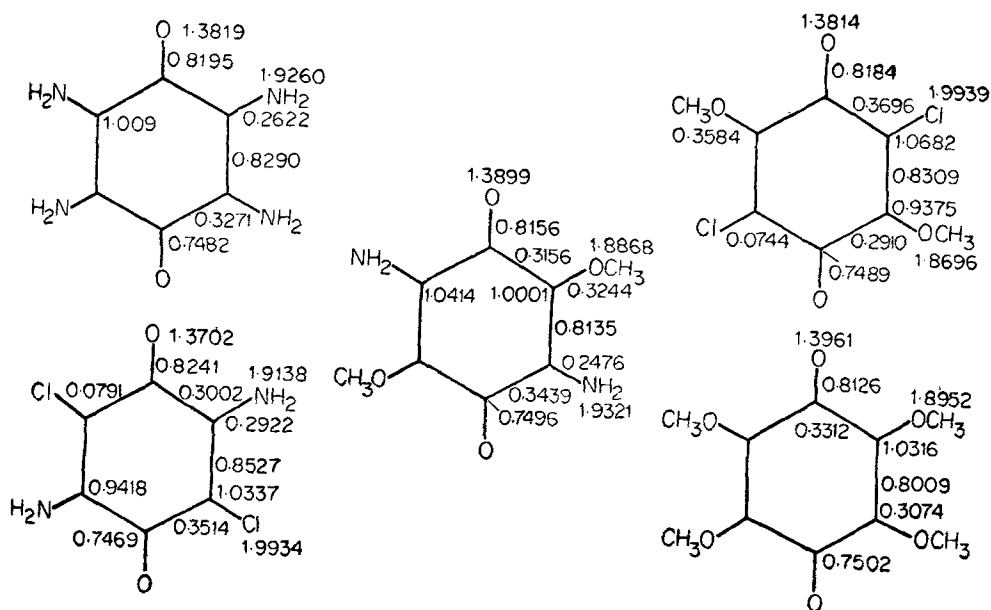


Figure 3. π -electron charge density of substituted quinones.

Acknowledgements

The authors wish to thank Prof. M D Karkhanawala of Bhabha Atomic Research Centre, Bombay and Prof. S Neelakantan of Madurai Kamaraj University for their encouragement. The authors also wish to thank Prof. C N R Rao of the Indian Institute of Science, Bangalore, for his helpful discussion.

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