

## ELECTRONIC ABSORPTION SPECTRA OF SOME 2, 5-DIALKYLAMINO-3, 6- DIBROMO-1, 4-BENZOQUINONE COMPOUNDS IN DIFFERENT ORGANIC SOLVENTS

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The UV-Visible spectra of 2, 5-diethylamino-(I<sub>a</sub>), 2, 5-di (β-hydroxyethylamino)- (I<sub>b</sub>), 2, 5-dibutylamino-(I<sub>c</sub>), and 2,5-dibenzylamino-(I<sub>d</sub>) 3, 6-dibromo-1, 4-benzoquinone were studied in ethanol, methanol, dioxane and chloroform. It is found that the high solvent polarity of ethanol and methanol plays no significant role on the quinonoid band position of the compound I<sub>a</sub> and I<sub>d</sub>. The charge transfer band of 2,5-dialkylamino substituent of the four compounds is blue shifted with increasing polarities of the solvent.

**Key words:** Electronic spectra, Benzoquinone derivatives, Solvent effect, UV study.

### Introduction

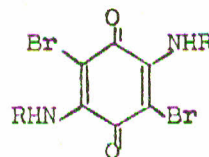
The electronic absorption spectra of quinones with condensed ring system and with heterocyclic nucleus have been studied by several authors [1-6]. The effect of substituents, solvents and pH's on the electronic spectral behaviour of p-benzoquinone and some of its derivatives have been reported [7-15]. Harfoush [9] has found that the spectra of p-benzoquinone derivatives commonly comprised two sets of bands. The first one at shorter wavelength due to π-π\* transitions within a benzenoid structure (phenyl ring of the polarised structure). The second series at longer wavelength corresponds to the π-π\* transition within the quinonoid structure (carbonyl and ethylenic systems). These bands displayed some changes in position and intensity on changing the substituents on the quinone nucleus or the polarity of the medium. The charge transfer bands shift to red with increasing polarity. The compounds 2, 5-dihydroxy-3-undecyl-, and 2,5-dihydroxy-1, 4- benzoquinone were used as reagents for detection of some drugs spectrophotometrically [13]. Very recently, the electronic absorption spectra of some new substituted diaminodibromo-1, 4- benzoquinones were investigated [15].

In this paper, the effect of ethanol, methanol, dioxane and chloroform on spectral behaviour of some 2, 5-dialkyl-amino-3, 6- dibromo-1, 4-benzoquinone compounds was studied.

### Experimental

The compounds I<sub>a-d</sub> were prepared [16] as follows: A mixture of tetrabromo-1, 4-benzoquinone [17] (0.05 mole) and relevant alkylamino (0.1 mole) was refluxed in excess of absolute ethanol for varying periods (0.5-10 hr) until bromanil has disappeared and a highly coloured solution or solid was formed. The reaction mixture was then cooled and the precipitated product was collected and recrystallized from appropriate solvent. The compounds were analyzed for their C, N, H

and Br contents (Table 1). The compounds have the general structure:



where R = C<sub>2</sub>H<sub>5</sub>(I<sub>a</sub>), -C<sub>2</sub>H<sub>4</sub>OH(I<sub>b</sub>), -C<sub>4</sub>H<sub>9</sub>(I<sub>c</sub>), -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>(I<sub>d</sub>).

The solvents used were all of spectral grade (BDH or E. Merck products). Stock solutions were prepared by dissolving the accurate weight of each compound in the appropriate volume of the required solvent. Solutions of lower concentrations were obtained by accurate dilution. The absorption spectra in the UV and visible regions were recorded with the aid of Shimadzu UV 200 S recording spectrophotometer using 1 cm matched silica cells.

### Results and Discussion

The electronic spectra of the parent compound 2, 5-diamino- 3, 6-dibromo-1, 4-benzoquinone was studied in chloroform, ethanol and ether by Issa *et al.* [6]. In chloroform only one band is observed at 338 nm, while in ethanol and ether two bands are observed, the first at 245 nm and the second at 338 nm in ethanol, and at 335 nm in ether. The bands at 335 nm and 338 nm are assigned to π-π\* transition of the quinonoid

TABLE 1. ANALYTICAL DATA OF PREPARED COMPOUNDS I<sub>a-d</sub>.

Compound	Colour	m.p. °C	Analysis%, Calcd. (Found)			
			C	H	N	Br
I <sub>a</sub> , C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> Br <sub>2</sub> O <sub>2</sub>	Dark violet	170	34.09 (34.08)	3.41 (3.27)	7.95 (8.00)	45.40 (45.62)
I <sub>b</sub> , C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>2</sub> Br <sub>2</sub>	Brownish violet	173	31.25 (31.07)	3.13 (3.21)	7.29 (7.30)	41.61 (41.46)
I <sub>c</sub> , C <sub>14</sub> H <sub>20</sub> O <sub>2</sub> N <sub>2</sub> Br <sub>2</sub>	Brown	198	41.16 (41.40)	4.90 (5.02)	6.86 (6.90)	39.15 (39.30)
I <sub>d</sub> , C <sub>20</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> Br <sub>2</sub>	Deep orange	183	50.40 (50.30)	3.36 (3.34)	5.88 (5.92)	33.56 (33.50)

system influenced by an intramolecular charge transfer. The band at 245 nm is assigned to  $\pi - \pi^*$  transition of the benzenoid structure.

Table 2 included the  $\lambda_{\max}$  and  $\epsilon_{\max}$  values of the characteristic absorption bands observed in the UV and visible

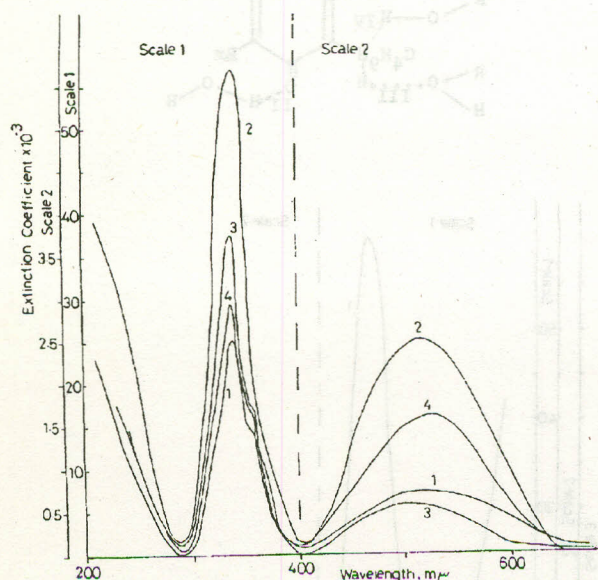


Fig. 1. Absorption spectra of 2,5-diethylamino-3,6-dibromo-1,4-benzoquinone ( $I_a$ ) in organic solvents: 1-Ethanol, 2-Methanol, 3-Dioxan, and 4- $\text{CHCl}_3$ .

spectra of the subjected compounds  $I_a - I_d$  ( $2 \times 10^{-5}$  mol.  $\text{dm}^{-3}$ ) in ethanol, methanol, dioxane and  $\text{CHCl}_3$ .

The spectrum of 2,5-diethylamino-3,6-dibromo-1,4-benzoquinone ( $I_a$ ) shown in Fig. 1, is characterized by three bands. The first band in each of the four solvents appeared at 340 nm and is assigned to the  $\pi - \pi^*$  transition of the quinonoid system [3,4] influenced by excitation of electrons on ethylenic groups. The second band appeared as a weak shoulder at 352-361 nm and is assigned to the  $\pi - \pi^*$  transition of the quinonoid nucleus greatly affected by an intramolecular charge transfer. This behaviour is common for  $\pi - \pi^*$  bands [18]. The third band is observed as a very broad band covering the range 430-620 nm and assigned to C.T. band taking place from the nitrogen atom of substituent:  $\text{NHC}_2\text{H}_5$  to the rest of molecule. This band is not observed in the spectrum of tetrabromo-1,4-benzoquinone [9], indicating that the C. T. band takes place as suggested from:  $\text{NHC}_2\text{H}_5$  of compound  $I_a$ . The observed blue shift in C. T. band on changing the solvent from  $\text{CHCl}_3$  to ethanol may be due to blocking of the carbonyl free electrons or the electrons of the donor substituent as represented below:

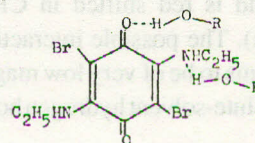
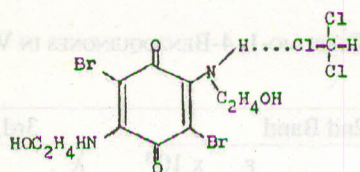


TABLE 2. ULTRAVIOLET ABSORPTION MAXIMA FOR 2,5-DIALKYLAMINO-3,6-DIBROMO-1,4-BENZOQUINONES IN VARIOUS ORGANIC SOLVENTS.

Compound	Solvent	1st Band		2nd Band		3rd Band	
		$\lambda_{\max}$	$\epsilon_{\max} \times 10^{-3}$	$\lambda_{\max}$	$\epsilon_{\max} \times 10^{-3}$	$\lambda_{\max}$	$\epsilon_{\max} \times 10^{-3}$
$I_a$ , $R = \text{NHC}_2\text{H}_5$	Ethanol	340	26.00	352sh	13.00	518	0.93
	Methanol	340	57.50	353sh	16.50	515	2.50
	Dioxan	340	37.50	361sh	13.50	508	0.60
	$\text{CHCl}_3$	340	29.50	357sh	16.00	524	1.67
$I_b$ , $R = \text{NHC}_2\text{H}_4\text{OH}$	Ethanol	354	59.90	—	—	511	0.77
	Methanol	356	20.20	—	—	515	1.25
	Dioxan	358	11.00	—	—	515	0.03
	$\text{CHCl}_3$	360	18.00	—	—	524	0.38
$I_c$ , $R = \text{NHC}_4\text{H}_9$	Ethanol	356	42.60	452	0.80	506	0.07
	Methanol	358	36.60	—	—	510	0.30
	Dioxan	358	36.90	—	—	515	0.27
	$\text{CHCl}_3$	362	28.80	—	—	527	0.24
$I_d$ , $R = \text{NHCH}_2\text{C}_6\text{H}_5$	Ethanol	350	35.90	456sh	1.61	500	1.47
	Methanol	350	57.80	450sh	0.08	500	0.15
	Dioxan	350	43.80	—	—	500	1.88
	$\text{CHCl}_3$	350	33.25	—	—	509	0.58

$\lambda_{\max}$ , nm,  $\epsilon_{\max}$ , mole $^{-1}$  cm $^2$ , sh = shoulder.

The electronic absorption spectra (Fig.2) of 2, 5-di ( $\beta$ -hydroxyethylamino)-3, 6-dibromo-1, 4-benzoquinone ( $I_b$ ) consists of two bands. The position and intensity of the first band is strongly influenced by the polarity of the solvent. This band is located at 354 nm ( $\epsilon = 59.90 \times 10^3 \text{ mole}^{-1} \text{ cm}^2$ ) in ethanol and at 360 nm ( $\epsilon = 18.00 \times 10^3 \text{ mole}^{-1} \text{ cm}^2$ ) in  $\text{CHCl}_3$  and assigned to  $\pi - \pi^*$  transition of the quinonoid part essentially the  $\text{C}=\text{O}$  groups [4] strongly influenced by an intramolecular CT. In dioxan, the band intensity is somewhat lower ( $\epsilon = 11.00 \times 10^3 \text{ mole}^{-1} \text{ cm}^2$ ) than the other solvents. Generally, the high extinction coefficient is a reliable indication of a CT band. The observed blue shift on changing the solvent from  $\text{CHCl}_3$  to ethanol may be explained on the basis that the  $\pi - \pi^*$  transition of the  $\text{C}=\text{O}$  group is influenced by an interaction with n-electrons [14]. The oxygen atom of  $\text{C}=\text{O}$  group can act as an acceptor for protons from ethanol molecules. This leads to blocking of the lone pairs on oxygen atoms which lowers the energy of the ground state of  $\text{C}=\text{O}$  groups. This increases the energy gap between the ground and excited states, hence a blue shift occurred. The second band of  $I_b$  at 511- 524 nm is assigned to pure CT transition from:  $\text{NHC}_2\text{H}_4\text{OH}$  to the rest of the compound. This band is red shifted in  $\text{CHCl}_3$  relative to ethanol (511-524 nm). The possible interaction between the solute and  $\text{CHCl}_3$  seems to be of very low magnitude and may take place through solute-solvent hydrogen bonding as shown:



This interaction facilitates the charge transfer from nitrogen atoms and consequently increases the residual negative charge which in turn enhances the charge migration.

In ethanol, the spectrum (Fig.3) of 2,5-dibutylamino-3, 6-dibromo-1, 4-benzoquinone ( $I_c$ ) consist of three bands, while in other solvents, two bands were observed. The first band at 356- 362 nm indicates that the position is influenced by the solvent polarity. The second and third bands in ethanol appeared at 452 nm and at 506 nm, respectively. The second band in other solvents appeared at 510-527 nm. These are assigned to  $\pi - \pi^*$  transitions of quinonoid system overlapped with  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$ , and to charge migration of electrons involved in:  $\text{NHC}_4\text{H}_9$ , respectively. The observed red shift on changing the solvent from ethanol the  $\text{CHCl}_3$  (356-362 nm, 506-527 nm) indicates that the interaction of  $\text{CHCl}_3$  with compound  $I_c$  takes place remote from the lone pair electrons located on the imino group. It is likely to occur between the hydrogen of:  $\text{NH}$  group and the chlorine atom of  $\text{CHCl}_3$ . In ethanol, and by similarity

with other systems [15,19-21], the following possible interactions are suggested:

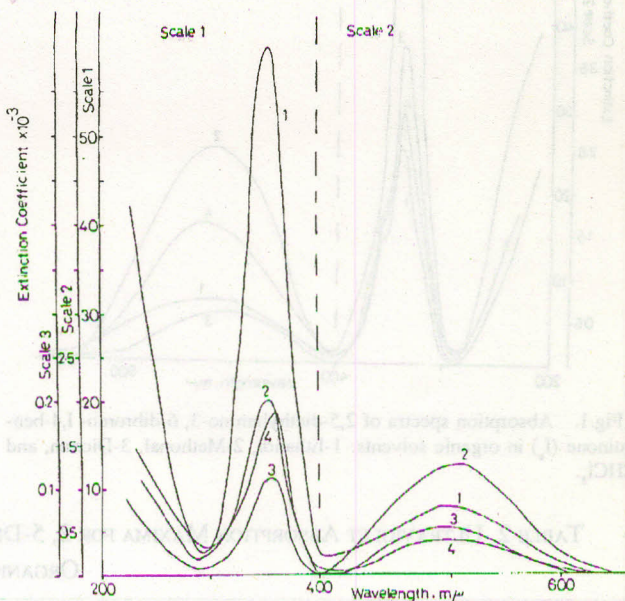
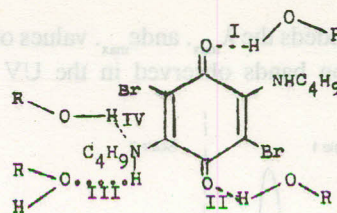


Fig. 2: Absorption spectra of 2, 5-di- ( $\beta$ -hydroxyethylamino)-3, 6-dibromo-1, 4-benzoquinone ( $I_b$ ) in organic solvents: 1-Ethanol, 2-Methanol, 3-Dioxan (scale 1, 3) and 4-  $\text{CHCl}_3$ .

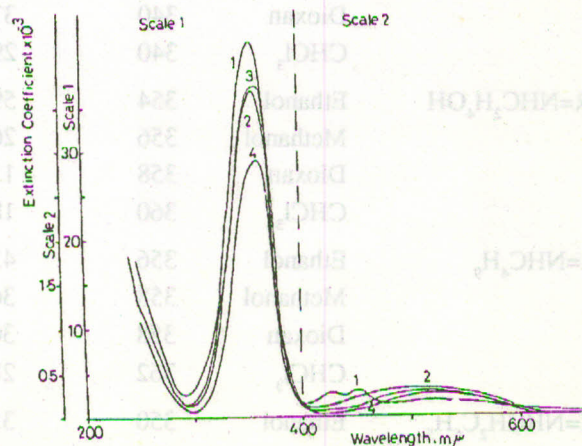


Fig. 3. Absorption spectra of 2,5-dibutylamino-3, 6-dibromo-1, 4-benzoquinone ( $I_c$ ) in organic solvents: 1-Ethanol, 2- Methanol, 3-Dioxan and 4- $\text{CHCl}_3$ .

Interaction I will favour the CT due to decreasing charges density on the C=O group as a result of blocking of its oxygen lone pairs. Interaction II is an intermolecular hydrogen bonding with the oxygen atom of the second C=O group. This facilitates the donation of the imino proton to an ethanol molecule attached in the third interaction. Interaction III is an intermolecular hydrogen bonding between an ethanol molecule and the proton on nitrogen atom. This will increase the CT due to increasing the residual negative charge on the nitrogen atom as a result of localization of the imino proton on the ethanol molecule. Interaction IV leads to blockings of the nitrogen lone pairs, hence retarding the intramolecular CT which is recommended for compound  $I_c$  where a blue shift is observed in ethanol relative to other solvents.

The electronic spectra of 2, 5-dibenzylamino-3, 6-dibromo-1, 4-benzoquinone ( $I_b$ ) in ethanol and methanol exhibits three bands, but in dioxan and  $CHCl_3$  two bands only. In the four solvents, the first band appeared at 350 nm with different intensities. It is mainly the  $\pi-\pi^*$  transition of the quinonoid structure overlapped with the transitions of the other groups. The second band in ethanol at 456 nm and in methanol at 450 nm is assigned to C=O and CT transitions. The third band at 500-509 nm in the four solvents, is assigned to pure CT transition originated from:  $NHCH_2C_6H_5$  as a good donor group. The observed change in intensity of the 350 nm band indicates that this band is actually due to a combination between C=C, C=O and CT transitions. The interference between the following possible interactions may increase or decrease the intensity of the band at 350 nm: (a) Interactions between the protons of  $CHCl_3$  and bromine atoms resulting a

decrease in the charge density on these centres, hence favouring the intramolecular CT. (b) Intramolecular CT from ethanol or methanol to the bromine atoms and vice versa is quite possible, and (c) Blocking the electrons of C=O group with ethanol or methanol resulting a blue shift which is not observed (Table. 2 and Fig.4.).

The validity of Beer's law is tested within the concentration ( $mol.dm^{-3}$ ) ranges  $(0.10-3.0)10^{-5}$  for  $I_a$ ,  $I_b$ ,  $(0.20-4.0)10^{-5}$  for  $I_c$  and  $(0.20-3.0)10^{-5}$  for  $I_d$ . Very good straight lines were obtained at two different wavelengths indicating that only one type of interaction is predominating namely the solute-solvent interaction, and no possible solute-solute association can take place.

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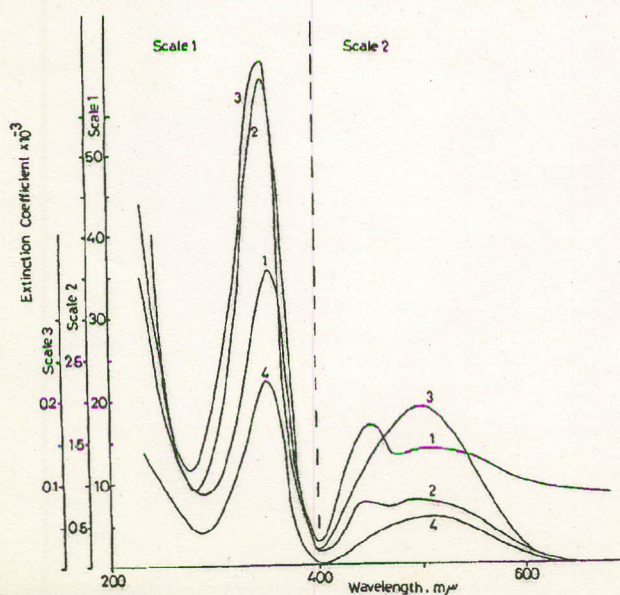


Fig. 4. Absorption spectra of 2, 5-dibenzylamino-3, 6-dibromo-1, 4-benzoquinone ( $I_b$ ) in organic solvents; 1-Ethanol, 2-Methanol (scales 1,3,) 3-Dioxan and 4- $CHCl_3$ .

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