

## Substitution and Solvent Effects on The UV Spectra of Chloro and Dichloroanilines

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The UV spectroscopic studies of chloro- and dichloroanilines have been made. The shift in the primary and secondary bands have been examined in the light of Doub and Vandenberg rule. The effect of substitution as well as the solvents have been explained in terms of electronic interaction within the molecules.

### INTRODUCTION

The spectroscopic behaviour (UV) of benzene ( $D_{6h}$ ) is not changed by reduction of symmetry due to substitution except for a shift in the positions of the bands<sup>1</sup>. Doub and Vandenberg<sup>2</sup> observed that the rule for disubstituted benzenes is a near constancy in the ratio of the shifts in the primary ( $1A_{1g} \rightarrow 1B_{1u}$ ) and the secondary ( $1A_{1g} \rightarrow 1B_{2u}$ ) bands  $\left( \frac{\Delta\lambda_{\text{secondary}}}{\Delta\lambda_{\text{primary}}} \approx 1.25 \right)$ . In the case of trisubstituted benzenes<sup>3</sup> they put forward the empirical rule that the spectrum of trisubstituted benzene contains the most shifted band of the disubstituted compounds. Each of the secondary or the first primary bands of the trisubstituted benzenes can be related to that band which is the most shifted among the corresponding bands in the constituent compounds. In the present work we have examined the UV spectra in the solution of chloro and dichloro anilines in the light of the above rule and the effect of changes in solvents.

### EXPERIMENTAL

The samples under investigation were obtained from Fluka, aniline, chloranilines (*ortho*, *meta* and *para*) and 2,3-dichloroaniline (DCA<sub>1</sub>), all liquids, were purified by distillation; 2,4-dichloroaniline (DCA<sub>2</sub>) and 3,5-dichloroaniline (DCA<sub>3</sub>), both solids, were recrystallised from ethanol. The solvents (cyclohexane, methanol and chloroform) were also distilled before use. A Hitachi (UV-VIS, model-320) double beam spectrophotometer with recording device (accuracy 0.1 nm) was used to record the spectra in the 200–400 nm region. The wavelength of maximum absorption ( $\lambda_{\text{max}}$ ), integrated absorption intensity ( $I_a$ ), obtained from the area under the curve  $\epsilon$  vs  $\bar{\nu}$ , and oscillator strength ( $f$ ) corresponding to both primary and secondary absorptions are presented in Table 1. Figure 1 contains representative samples of spectra of DCA's in methanol.

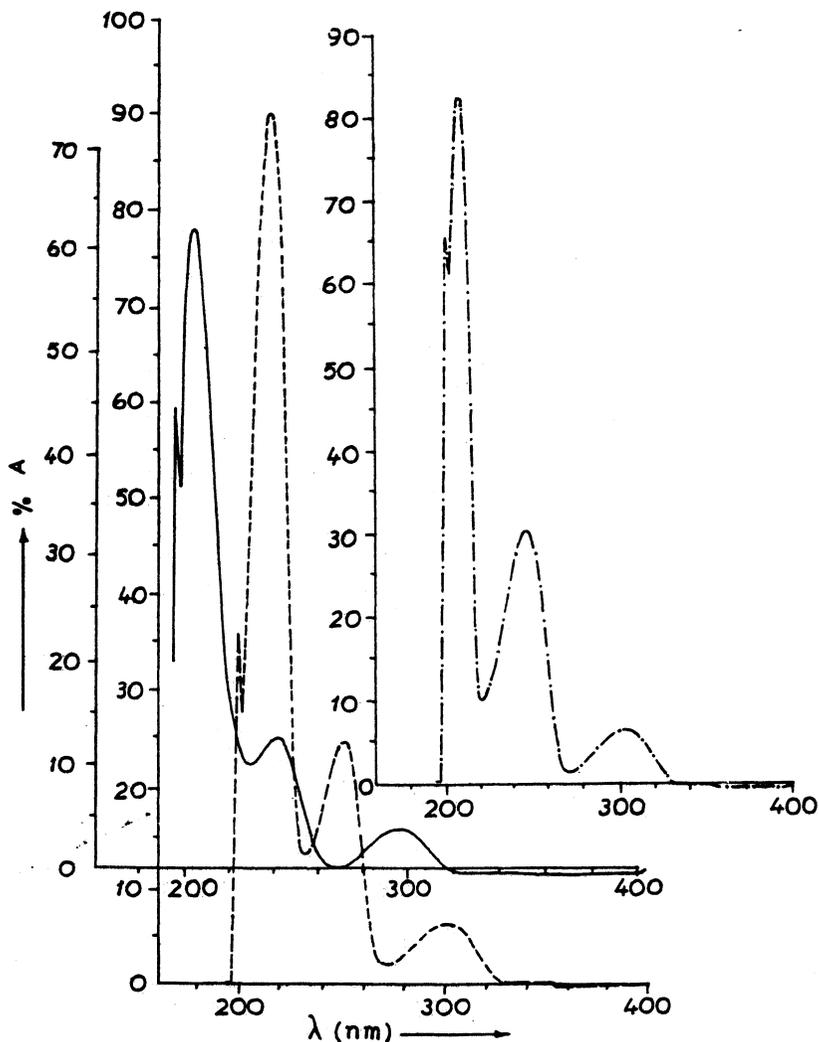


Fig. 1

- U.V. Spectrum of 2,3-Dichloroaniline in Solvent Methanol.  
 --- U.V. Spectrum of 3,5-Dichloroaniline in Solvent Methanol.  
 - · - · U.V. Spectrum of 2,4-Dichloroaniline in Solvent Merhanol.

## RESULTS AND DISCUSSION

The values of  $\Delta\lambda_1$  and  $\Delta\lambda_2$  (displacement of the primary and secondary bands respectively relative to those in benzene) of the aniline, chloroanilines and dichloroanilines are given in Table 2. One more intense band is expected to occur

in each of the isomers at a much lower wavelength (second primary band) but the instrument used does not allow measurements in that region (below 200 nm). The long wavelength and low intensity bands (e.g. the 280 nm of aniline) are identified as the secondary bands. According to Table 2 the  $\Delta\lambda_2$  is approximately proportional to  $\Delta\lambda_1$  (except in the case of DCA<sub>2</sub>). This regularity confirms that the two absorption bands in each derivative arise from the same chromophore (benzenoid origin) and none from -NH<sub>2</sub> or -Cl substituents (that would involve n-electrons).

TABLE 1  
RESULTS OF THE ELECTRONIC ABSORPTION SPECTRA OF THE THREE  
ISOMERIC DICHLOROANILINES FOR THE PRIMARY AND SECONDARY BANDS

Compound	Solvent	$\nu_m(\text{cm}^{-1})$	$\epsilon_{\text{max}}$	$I_a$	f
Primary Band					
DCA <sub>1</sub>	Methanol	41,500	979.9	$0.343 \times 10^7$	0.0148
DCA <sub>2</sub>	Methanol	41,500	2610.6	$1.066 \times 10^7$	0.0460
DCA <sub>3</sub>	Methanol	40,500	2042	$1.85 \times 10^7$	0.0368
Secondary Band					
DCA <sub>1</sub>	Methanol	34,500	250.6	$0.075 \times 10^7$	0.0032
DCA <sub>2</sub>	Methanol	32,500	470	$0.1746 \times 10^7$	0.0076
DCA <sub>3</sub>	Methanol	33,550	455	$0.1552 \times 10^7$	0.0067

TABLE 2

Compound	Solvent	$\lambda_{\text{max}}(\text{nm})$ (Primary)	$\lambda_{\text{max}}(\text{nm})$ (Secondary)	$\Delta\lambda_1$ (nm)	$\Delta\lambda_2$ (nm)	$\frac{\Delta\lambda_1}{\Delta\lambda_2}$
DCA <sub>1</sub>	Cyclohexane	239	292	35	36	0.97
DCA <sub>2</sub>	Cyclohexane	243	301	39	45	0.86
DCA <sub>3</sub>	Cyclohexane	242	292	38	36	1.05
Aniline <sup>1</sup>	Cyclohexane	230	280	26	24	1.08
<i>o</i> -Chloroaniline	Cyclohexane	233	287	29	31	0.93
<i>m</i> -Chloroaniline	Cyclohexane	238	290	34	34	1.00
<i>p</i> -Chloroaniline	Cyclohexane	242	298	38	42	0.90
DCA <sub>1</sub>	Methanol	242	297	38	41	0.92
DCA <sub>2</sub>	Methanol	244	304	40	48	0.83
DCA <sub>3</sub>	Methanol	248	300	44	44	1.00
DCA <sub>1</sub>	Chloroform	243	294	39	38	1.02
DCA <sub>2</sub>	Chloroform	245	303	41	47	0.87
DCA <sub>3</sub>	Chloroform	247	296	43	40	1.07

Primary  $\lambda_{\text{max}}$  for benzene<sup>1</sup> = 204 nm

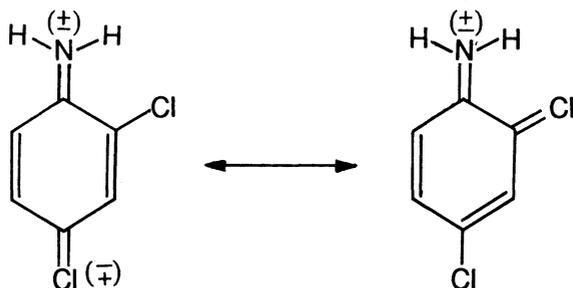
Secondary  $\lambda_{\text{max}}$  for benzene<sup>1</sup> = 256 nm

$\Delta\lambda_1$  = Relative shift of primary  $\lambda_{\text{max}}$  with respect to that of benzene

$\Delta\lambda_2$  = Relative shift of secondary  $\lambda_{\text{max}}$  with respect to that of benzene

The bands in *para*-chloro-aniline (242 and 298 nm) are more displaced than

those in *ortho*-chloroaniline (233 and 287 nm) and *meta*-chloroaniline (238 and 290 nm) while the two bands in DCA<sub>2</sub> appear at 243 and 301 nm. This is in conformity with the Douv-Vandenbelt rule. Qualitatively the displacement of bands may be explained in terms of electronic interaction in which resonance rather than coulombic displacement prevails. In the case of disubstitution the displacement is maximum when both substituents have different directional characters and are in *para* position. In the case of trisubstitution in none of the present isomers except the DCA<sub>2</sub> two groups are in *para* position to each other and we have two electron withdrawing atoms as against one in chloranilines. If the absorption of light is considered to be associated with charge separation resonance in the excited state the DCA<sub>2</sub> will have the following resonating



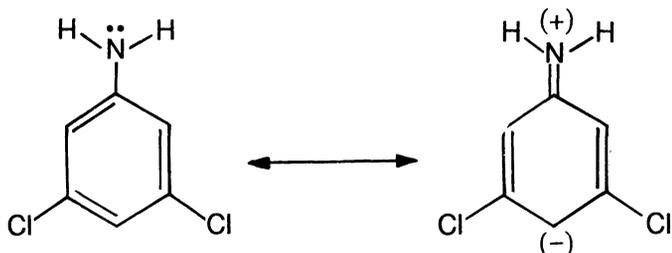
structure in which the effect of one of the chlorine atoms is limited to electrostatic contribution and not in resonance so that these structures should not be far removed in energy from those of the *para*-chloroaniline. Therefore in the spectra of the trisubstituted DCA<sub>2</sub> the primary and secondary bands should not be far displaced from the corresponding bands in *para* chloroanilines. Such structures are possible because nitrogen can share more than a pair of electrons with the benzene ring and can accommodate a positive charge. Chlorine has both properties, *i.e.*, withdrawing and releasing electrons. Hence it can also share more than a pair of electrons with the benzene and accommodate a positive charge. Thus a single structural concept, *i.e.*, partial double bond formation C=NH<sub>2</sub> and C=Cl helps to account for the observed facts.

Structures of this type are not possible in DCA<sub>1</sub> and DCA<sub>3</sub> for which the bands are appreciably red-shifted with respect to *ortho*- and *meta*-chloroanilines. In these cases the presence of two chlorine atoms may enhance the electrostatic contribution leading to enhanced polarisation of the excited state and its stabilisation by interaction with solvents.

### Effect of Solvents

In the case of anilines earlier investigations<sup>4-6</sup> indicate that changing from non-polar to polar solvents causes blue shift and decrease in the value of molar extinction. In the present case the trisubstituted derivatives show definite red shift of the first primary band. The intensity of the primary band also decreases by changing from non-polar to polar solvents. This shows that (i) the excited state is more polar, and (ii) the polar forms contribute little to the resonance structure.

Polarised structure in the excited states of the dichloroanilines may be deduced by assuming that one of the non-bonding electrons of the N-lone pair is excited to the higher energy antibonding molecular orbital leading to the following resonance forms in the excited states.



The red shift is more pronounced in case of DCA<sub>1</sub> and DCA<sub>3</sub> rather than DCA<sub>2</sub>. In the case of DCA<sub>2</sub> one atom of chlorine is at the *para*-position with respect to the -NH<sub>2</sub> group which therefore results in greater dipole moment than DCA<sub>1</sub>. Hence the interaction with the polar solvents results in stabilisation of both the ground state and excited state almost to the same extent. On the other hand, DCA<sub>3</sub> (a more symmetric molecule) has lower dipole moment than DCA<sub>2</sub>. Naturally the solute-solvent interaction is more in the excited state than in ground state resulting in greater stabilisation of excited state.

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(Received: 16 December 1992; Accepted: 1 May 1993)

AJC-608