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Effect of Solvents and pH Variation on Electronic Spectra of Dichloro-Nitroanilines

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Electronic spectra in various polar solvents have been recorded in the region 2000 to 4000 Å. The effect of change of solvent on electronic transition of 2,4-dichloro-6-nitro- and 4,5-dichloro-2-nitroanilines is explained. The effect of pH variation has also been studied.

INTRODUCTION

Solvent effects on electronic absorption spectra of nitroaniline have been reported by many workers[1–3]. But no work appears to have been carried out on the halogeno substituted nitroanilines. The present paper reports the solvent effect on the electronic spectra of 2,4-dichloro-6-nitroaniline and 4,5-dichloro-2-nitroaniline. The effects of pH variation have also been discussed on electronic spectra of these molecules.

EXPERIMENTAL

The spec-pure compounds 2,4-dichloro-6-nitroaniline and 4,5-dichloro-2-nitroaniline (2,4,6-DCNA and 4,5,2-DCNA respectively) (Fig. 1) were obtained from M/s EGA Chemie (West Germany) and were used as such. Their purity was confirmed by elemental analysis and melting point determination. The electronic spectra of these molecules were recorded in various solvents on spectrophotometer Beckmann Model M-35. The pH values measured with a Systronics digital pH meter Model-335.

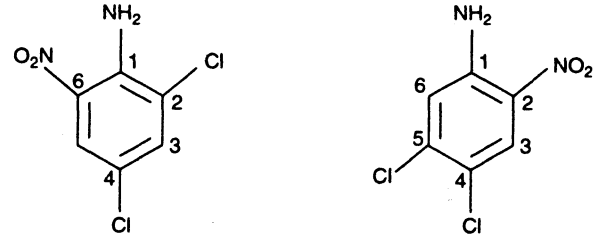

Fig. 1. The structural diagrams of (i) 2,4,6-DCNA, (ii) 4,5,2-DCNA

RESULTS AND DISCUSSION

The effect of solvents on electronic transitions of these molecules are given in Table-1 while electronic transition and pH variation are given in Table-2. The near ultraviolet absorption spectra of 2,4,6-DCNA and 4,5,2-DCNA in various solvents are shown in Figs. 2 and 3 respectively while the absorption spectra of these molecules in various solvents at different pH are shown in Figs. 4 and 5. The spectrum of 4-nitroaniline shows two intense bands in the accessible ultraviolet region. One band appears at λ_{max} 375 nm and the other at 227 nm in ethanol sulution[1, 2]. The first band at 375 nm is probably an intermolecular charged transfer band due to a transition accompanied with a partial electron transfer from the electron donating amino group to the electron-accepting nitro group through the system of benzene ring. The steric effect on this band was studied by Arnold and coworkers.[3, 4]

The band observed at 238 nm corresponds to $A_1 \rightarrow B_2$ transition in nitroaniline[5] and is derived from the $A_{1g} \rightarrow B_{1u}$ transition on lowering the symmetry from $D_{\infty h}$ to C_{2v}. According to Clark and Tinocco[6] bands at 210 nm and 200 nm corresponds to $A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow A_{1u}$ transitions respectively. The bands are weak as the said transitions are forbidden but they are understood to occur as a the result of coupling with variation of suitable symmetry[4]. According to Dyer[7] molecules which contain non-bonding electrons containing —NH_2 groups, there occurs a band around 210 nm which corresponds to n-π^* transition.

The π-π^* undergoes a red shift with increasing solvent polarity[8]. This may be attributed to the momentary polarisation of the solvents by transition dipole of the solute[9]. It can be seen from Table-1 that there is a pronounced red shift in the π-π^* transitions of the present substituted nitroanilines with increasing the polarity solvents.

In the present study a blue shift in n-σ^* transition is observed as the solvent is changed from benzene to water which is in accordance with the above stated fact (Figs. 2 and 3; Table-1). Yadav *et al.*[10] noted a marked red shift in n-π^* transitions with increasing refractive index of solvents.

TABLE-1
EFFECT OF SOLVENTS ON ELECTRONIC TRANSITIONS OF 2,4,6-DCNA AND 4,5,2-DCNA

Solvent	RI	DC	2,4,6-DCNA				4,5,2-DCNA			
			I n-π^*	II n-π^*	π-π^*	n-σ^*	I n-π^*	II n-π^*	π-π^*	n-σ^*
Benzene	1.5236	2.3	371	278	—	—	368	277	—	—
Chloroform	1.4580	4.5	358	290	—	—	360	285	—	—
Ethanol	1.3773	25.0	352	268	235	200	350	274	240	200
Methanol	1.3662	32.5	347	265	240	205	355	268	245	200
Water	1.3380	80.5	330	260	—	—	330	265	—	—

where DC = dielectric constant,
RI = refractive index

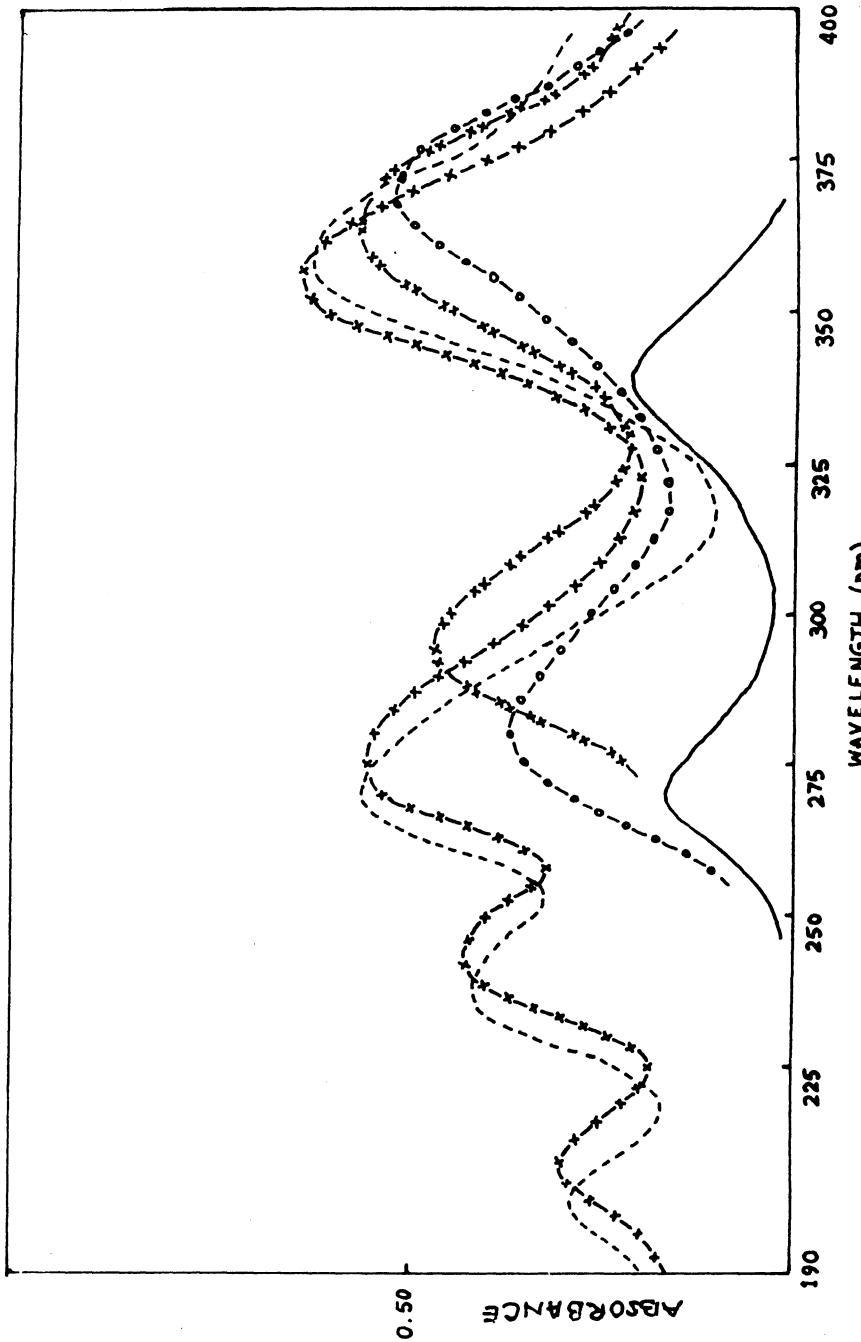

Fig. 2. Ultraviolet absorption spectra of 2,4-dichloro-6-nitroaniline in (–) water, (- -) ethanol, (–x–x–) methanol, (–O–O–) benzene, (–xx–xx–) chloroform.

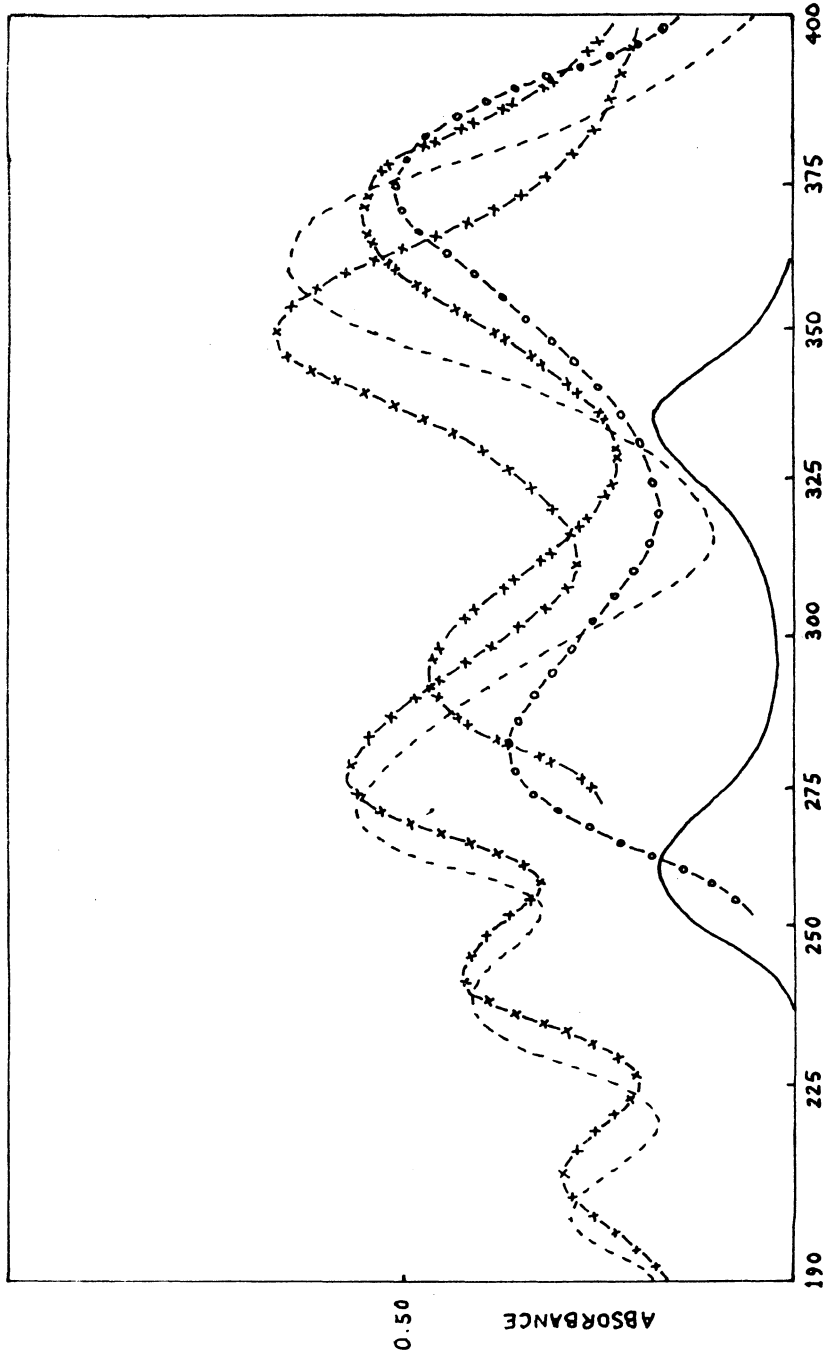

Fig. 3. Ultraviolet absorption spectra of 4,5-dichloro-2-nitroaniline in (–) water, (- -) ethanol, (–x–x–) methanol, (–O–O–) benzene, (–xx–xx–) chloroform.

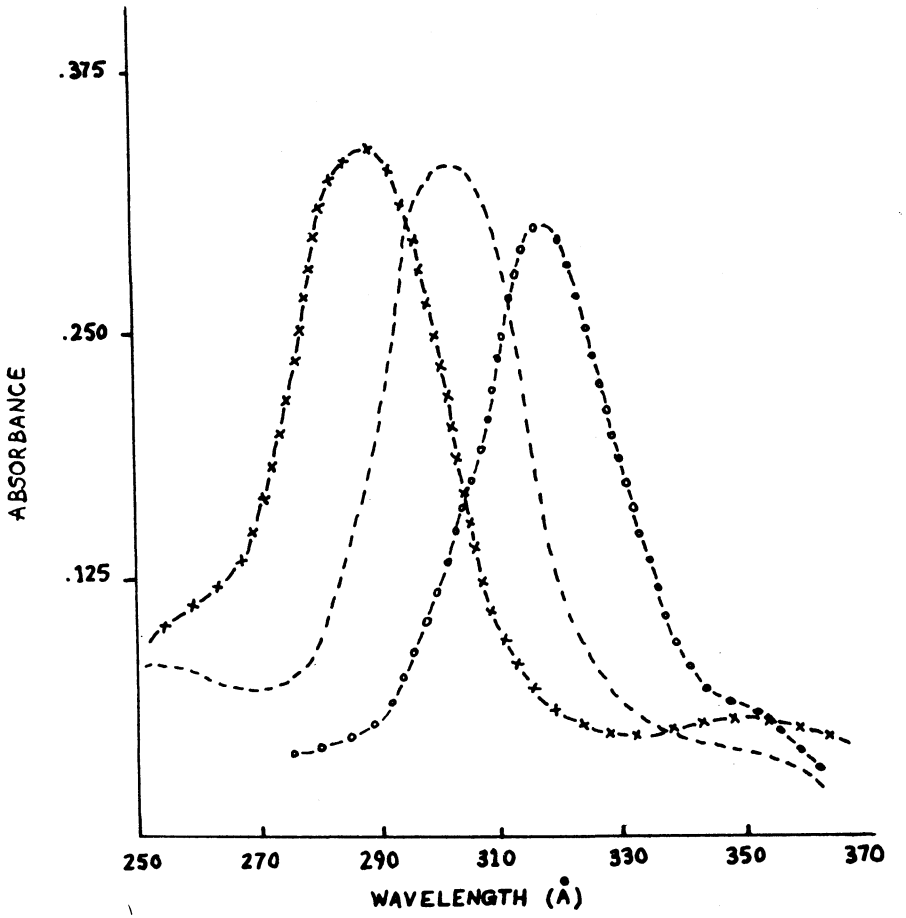

Fig. 4. Ultraviolet absorption spectra of 2,4-dichloro-6-nitroaniline in ethanol (– – –) neutral, (–x–x–) acidic and (–O–O–) alkaline medium

TABLE-2
n-π* TRANSITIONS AND EFFECT OF pH IN 2,4,6-DCNA AND 4,5,2-DCNA

Solvent	RI	2,4,6-DCNA		4,5,2-DCNA	
		pH	n-π*	pH	n-π*
Ethanol	1.3773	6.8	302	6.4	300
Ethanol + HCl		2.2	288	2.8	291
Ethanol + NaOH		12.3	316	11.9	314
Methanol	1.3362	7.1	300	6.9	303
Methanol + HCl		1.9	285	2.3	298
Methanol + NaOH		11.9	319	11.2	313

where RI = refractive index.

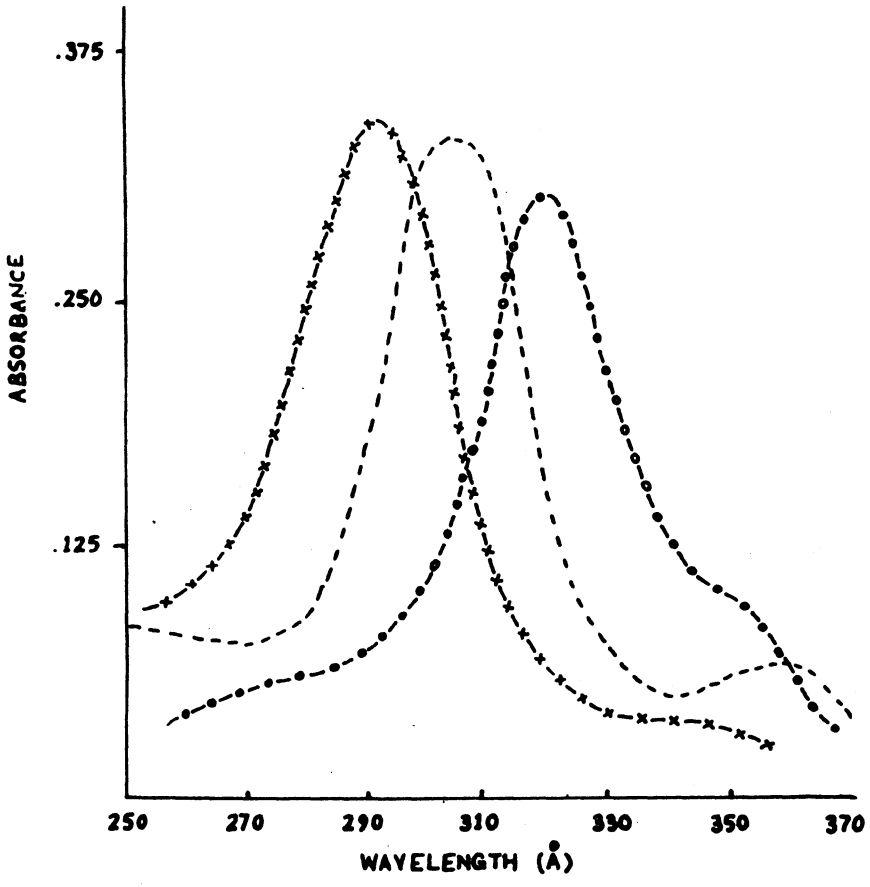

Fig. 5. Ultraviolet absorption spectra of 2,4-dichloro-6-nitroaniline in methanol (–) neutral, (–x–x–) acidic and (–o–o–) alkaline medium

Effect of pH variation of electronic transitions

Since the interpretation of spectral measurements to a considerable extent mainly depends on the choice of sites of localization of protons, the question of possible effect of pH variation on electronic transitions of the compounds under study is very important.

The substituents such as —OH have an electron-withdrawing inductive effect but they exert an electron donating mesomeric effect from *ortho* and *para* position. However, it is the position of hydroxy group which affects the spectral shifts dominantly due to its more active and electron-donating nature. In the present study a red shift is observed with decrease in pH and a blue shift with increase in pH in $n–\pi^*$ transition in the compound becomes broader by the addition of acid; therefore it is difficult to identify the exact position corresponding to the main peak.

In the case of nitroanilines, there is a blue shift in the position of entire band

with decrease in pH, the n-π^* band is reported to the shifted towards shorter wavelength in acidic solution by many workers[11]. Becker *et al.*[8] have suggested a blue shift of the n-system in a strong acid solution due to the binding of nonbonded electrons by protonation. In accordance with the above, we have also observed a blue shift in n-π^* band with the addition of acid in the aqueous solutions of 2,4,6-DCNA and 4,5,2-DCNA as the neutral form changes to acidic form or alkaline form (Fig. 4 & 5); with the increase in pH a large red shift is observed in the n-π^* transitions of these molecules. Mason *et al.*[12] have observed a red shift with the increase in pH in 6-hydroxy quinoline.

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