

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 7, July 2017

Spectrophotometric Studies on the Charge Transfer Interaction of 4-Nitroquinoline-1-Oxide with some π –and n-Donors

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ABSTRACT: 4-Nitroquinoline-1-oxide (4-NQO) is a carcinogenic compound. In this paper the charge transfer interaction between acceptor 4-NQO and donors like π –donors (benzene, Toluene, *p*-xylene) and n-donors (Aniline, N, N-Dimethyl aniline and Pyridine) has been studied with the help of spectrophotometric studies.

KEYWORDS: 4-NQO, π –donors (benzene, Toluene, *p*-xylene) and n-donors (Aniline, N, N-Dimethylaniline and Pyridine), Spectrophotometric studies, Cancer, Charge transfer interaction.

I. INTRODUCTION

It is now a truism that the chemistry of charge transfer complexes has experienced an impressive renaissance.^{1,2,3,4} The stability of molecular complexes which mainly occurs through interaction between donor and acceptor may play an important role in understanding several fundamental mechanisms involved in the chemical initiation of some dreadful diseases in the biological system, the conformation of proteins and nucleic acids,^{5,6} the role of drug interaction,⁷ the mechanism of toxicity^{8,9} as well as carcinogenicity^{10,11,12,13} of pesticides.^{14,15} The formation of charge transfer complexes between some π -donors and 4-NQO (π -acceptor) have been investigated through differential refractometric and conductometric techniques. A probable model on these interactions has been proposed, but definite site of interaction requires additional evidence. In order to provide additional evidence on the definite site of interaction on these charge transfer complexation processes and to study the role of charge transfer complexes in the chemical initiation of cancer¹⁶ on molecular level, the interaction of 4-NQO with

some π -donors (benzene, toluene, *p*-xylene) and n-donors (aniline, N, N-dimethylaniline, pyridine) have been studied spectrophotometrically in polar (chloroform) and nonpolar (carbon tetrachloride) solvents.

II. EXPERIMENTAL (Materials)

4-Nitroquinoline-1-oxide was obtained commercially from Sigma. It was recrystallized before use. The donors (benzene, toluene, *p*-xylene, aniline, N, N-dimethylaniline, pyridine) were dried and purified. The analytical reagent grade benzene was satisfactory for most purposes. If required it was dried. It first treated with anhydrous calcium chloride, filtered, and then placed over sodium wire. Toluene, free from Sulphur compounds was purchased. It was similarly dried. The AR grade pyridine was employed. Aniline was dried over potassium hydroxide for 24 hrs. Then redistilled which gave a colorless liquid. If it has color on distillation or if it gives colored liquid, then it is treated with

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Zn dust and redistilled to give a colorless liquid. P-Xylene was dried over molecular sieves and then redistilled. Chloroform and carbon tetra- chloride used were of analytical grade. The purification procedure for all above noted chemicals were essentially the same as reported in the literature.¹⁷

III. PREPARATION OF THE SOLUTION AND ELECTRONIC SPECTRAL MEASUREMENT

Stock solutions of donors and the acceptors were prepared by weighing on an analytical balance and subsequent dilution to the required volume in volumetric flask in chloroform or carbon tetra- chloride. The solutions employed for the spectrophotometric measurements were prepared from stock solutions by pipetting the calculated volumes into 10ml volumetric flask. All stock solution were freshly made on the day of measurement. The measurement of the spectra were made on a Bousch and Lomb Spectronic-2000 spectrophotometer using 1 cm quartz cell (31°C), The spectra were run in the region 500-300 nm using 1 cm path length cell and scan time was 2 minutes. Optical densities were reproducible at least to 0.1%. The spectral studies were performed by keeping the acceptor concentration constant and donor concentration was varied. The spectra were recorded immediately after mixing donor and acceptor solutions. Since 4-NQO absorbs strongly in visible region, the charge transfer band appeared as a shoulder with acceptor band. Thus, difference spectral studies were made by taking spectra of the solution (donor and acceptor) versus solution of 4-NQO of equal concentration in the same solvent.

Since 4-NQO is a potent carcinogen^{18,19,20,21} gloves were used in handling the solution and the volumes were measured by using glass tuberculin syringes. The waste material was collected for spectral disposals.

IV. RESULTS AND DISCUSSION

4-Nitroquinoline-1-oxide (acceptor) absorbs at 250 nm (ϵ 16.66) and 370nm (ϵ 7.14) due to $\pi - \pi^*$ & n- π^* transition respectively. The π -donors absorb in this region 243-275 nm ($^1B_{2u} \leftarrow ^1A_{1g}$ transition) whereas n-donors absorb in the region 235-288 nm ($^1B_{2u} \leftarrow ^1A_{1g}$). The spectra of charge transfer complexes of benzene + 4-NQO, toluene + 4-NQO, p-xylene + 4-NQO solution with varying concentration of donors and at the constant concentration of the acceptor were recorded. On interaction of donors with acceptor, the appearance of new absorption band in the region 409-418 nm has been observed in case of almost all compounds studied (table 1.1). This new absorption band has been interpreted as the charge transfer band of the molecular complex resulting from the interaction of 4-NQO with π -electron pool of the donors.

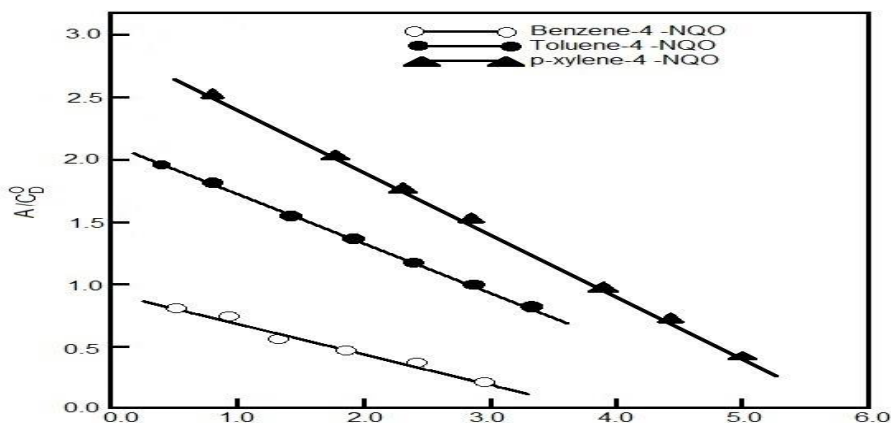


FIG. 1.1 Plots of A/C_0 for molecular complexes of Benzene, Toluene, p-xylene and 4-NQO complexes in Chloroform

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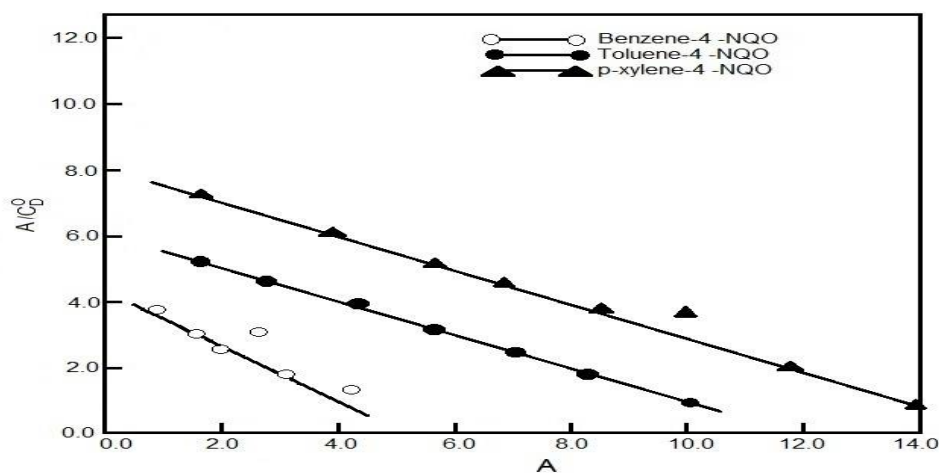


FIG. 1.2 Plots of A versus A/C_D^0 for Benzene, Toluene, p-xylene for molecular complexes with 4-NQO in Carbon tetrachloride.

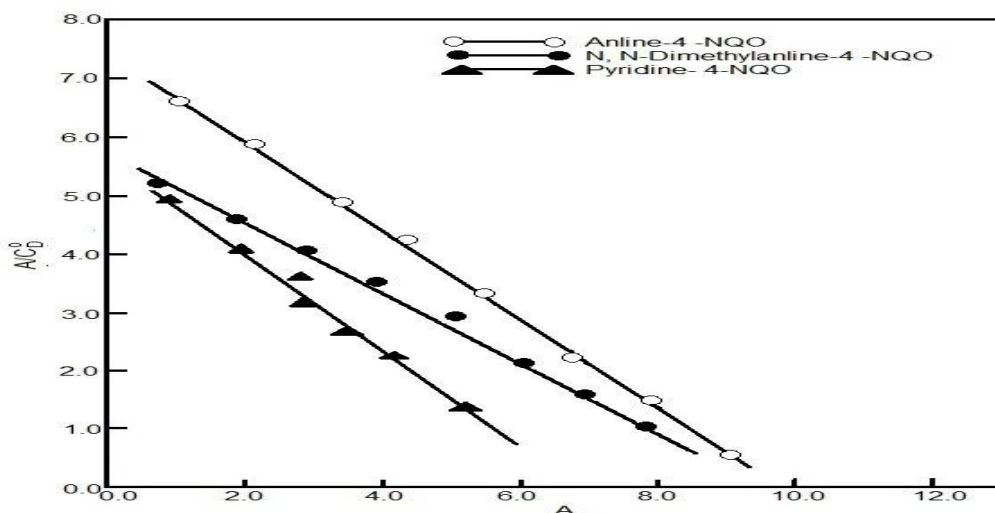


FIG. 1.3 Plots of A versus A/C_D^0 for molecular complexes of Aniline, N, N-Dimethylaniline, Pyridine and 4-NQO complexes in Chloroform.

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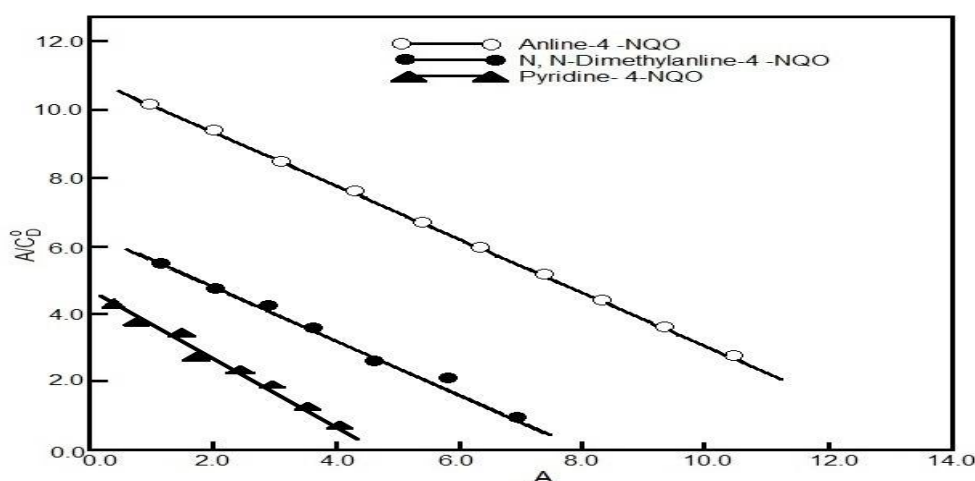


FIG. 1.4 Plots of A versus A/C_D^0 for Aniline, N, N-Dimethylaniline pyridine for molecular complexes with 4-NQO in Carbon tetrachloride.

Table 1.1 The Charge Transfer Band and Calculated Data for 4-NQO Complexes with some π — and n-Donors

Donor	Solvent	Concentration range of Donor*	λ_{max} (C.T.) (nm)	K_1 ($\text{dm}^3 \text{mol}^{-1}$)	$\epsilon \times 10^{-4}$
Benzene	CHCl_3	0.6-12.0 M	415.5	0.21 ± 0.01	2.1
	CCl_4	0.3-2.7 M	409.0	0.36 ± 0.01	2.9
Toluene	CHCl_3	0.3-4.5 M	416.0	0.41 ± 0.01	2.7
	CCl_4	0.4-6.0 M	410.3	0.50 ± 0.02	3.0
p-Xylene	CHCl_3	0.4-8.0 M	417.5	0.48 ± 0.02	3.1
	CCl_4	0.3-7.0 M	412.5	0.60 ± 0.03	3.5
Aniline	CHCl_3	0.2-8.0 M	421.5	0.72 ± 0.02	5.01
	CCl_4	0.1-3.3 M	415.9	0.80 ± 0.02	6.85
N, N-Dimethyl-aniline	CHCl_3	0.2-8.0 M	416.0	0.60 ± 0.03	4.81
	CCl_4	0.2-7.0 M	410.5	0.70 ± 0.02	5.2
Pyridine	CHCl_3	0.2-4.0 M	418.0	0.92 ± 0.02	3.25
	CCl_4	0.1-4.0 M	410.0	1.00 ± 0.04	4.12

*The concentration of the acceptor (4-NQO) was kept constant at $\text{ca. } 2 \times 10^{-4} \text{ M}$ in each case.

The spectra of aniline + 4-NQO²², N, N-dimethylaniline + 4-NQO²³, pyridine + 4-NQO²⁴ solution with different concentrations of donors and at the constant concentration of acceptor were recorded. The region 415.9-418.0 nm is clearly seen from this table (Table 1.1). The equilibrium constant data, K_1 and molar extinction coefficient, ϵ , of complexes have been calculated by using these values are listed in Table 1.1. The K_1 value of N, N-dimethylaniline: 4-NQO complex^{25,26,27} is less than aniline: 4-NQO complex.^{28,29} This may be due to the steric hindrance caused by two

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$$h\nu_{CT} = I - (EA - E) + \frac{C_1}{I - (EA - E)} \quad \dots (1.1)$$

methyl groups present on N-atom of aniline. According to Mulliken's theory of intermolecular interaction between electron-acceptor and electron-donor molecules, the energy $h\nu_{CT}$ of electron transfer from donor to acceptor is related to the ionization potential, I , of the donor and electron affinity, EA , of the acceptor by expression:^{2,4,9} C_1 where E is mainly the energy of the coulomb attraction between D^+ and A^- after the transfer of one electron from the donor D to the acceptor A and C_1 is constant. At sufficiently large ionisation potential ($I > 7.5$ eV)¹⁰ the last term in the above expression may be neglected and the equation reduces to,

$$h\nu_{CT} = I - (EA - E) \quad \dots (1.2)$$

For the charge transfer of the same bond type and configuration E may be considered constant and for two donors of almost similar structure and one and the same acceptor the following relationship is applicable:

$$(h\nu_{CT})_1 - (h\nu_{CT})_2 = I_{(1)} - I_{(2)} \quad \dots (1.3)$$

The ionization potential of donor (2) can be calculated from charge transfer energies of complexes of donor (1) and donor (2) with the same acceptor if the ionization potential of donor (1) is known. Using Eq. (1.3), the ionization potential of benzene, toluene, p-xylene, aniline, N,N-dimethylaniline and pyridine have been calculated and these values were plotted against $h\nu_{CT}$. A linear plot for each donor system was obtained (Figs. 1.1, 1.2, 1.3, 1.4, 1.5, 1.6). Similar results for other systems have also been reported in the literature.^{30,31,32}

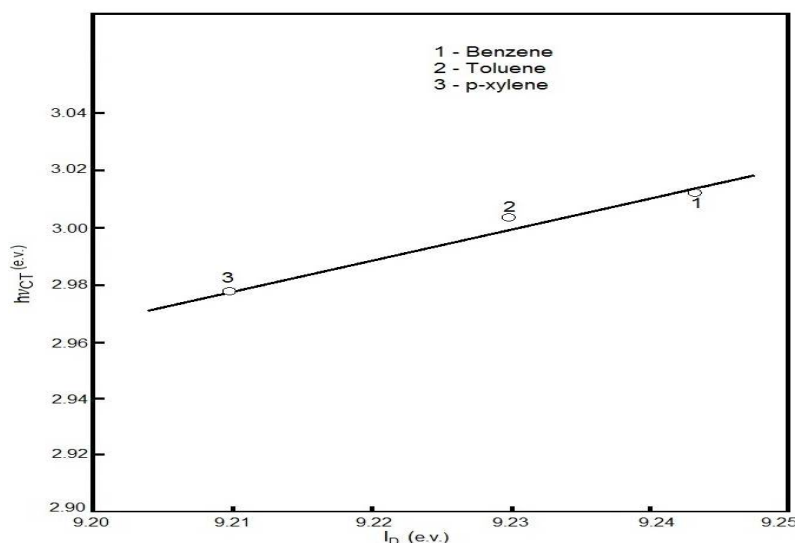


FIG. 1.5 Dependence of the transition energy, $h\nu_{CT}$, upon the ionization potential of the donor, I_D , for complexes of 4-NQO

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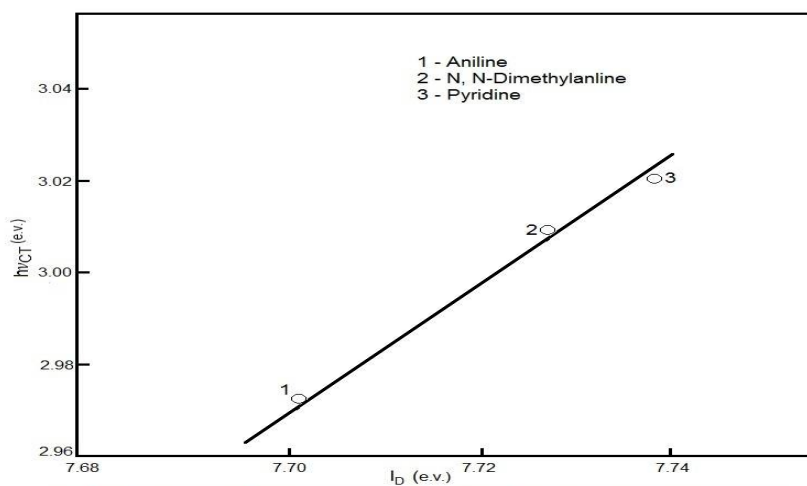


FIG. 1.6 Dependence of the transition energy, $h\nu_{CT}$, upon the ionization potential of the donor, I_D , for complexes of 4-NQO.

V. CONCLUSION

Cancer is defined as a disease of multicellular organism which is characterized by the seemingly uncontrolled multiplication and speed with in the organism of apparently abnormal forms of the organism's own cells. In this paper the interaction of 4-NQO (acceptor) with some π -donors (benzene, toluene, p-xylene) and n-donors (aniline, N, N-Dimethylaniline, pyridine) have been studied spectrophotometrically. The carcinogenicity of 4-NQO is great importance because it's potency to produce cancer is comparable to the most potent aromatic hydrocarbons, nucleic acid, bases as well as with proteins. By this interaction the normal functions of the cell become disturbed leading towards the abnormality in the function of the cell. This abnormality may later on appears in the form of mutagenesis which transforms into carcinogenesis.

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