CNDO/SCF MOLECULAR ORBITAL STRUCTURAL STUDIES AND CHARGE TRANSFER COMPLEX FORMATION BETWEEN 4,4'-DIMETHOXYDIQUINONE AND URACIL

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ABSTRACT. Through CNDO/SCF molecular orbital calculations, the structure of 4,4'-dimethoxy-diquinone (DQ) has been discussed and compared with some related compounds. The electron transfer between DQ and uracil was studied in ethanol as an interaction medium. The ionization potentials and the electron affinities of the studied molecules have been calculated in addition to their charge densities giving the columbic potential energy of the donor and acceptor. The experimental charge transfer band lies at 500 nm. The electronic transitions have been calculated for the singlet and triplet transitions in uracil and DQ molecules using the SCF eigenvectors of the two HOMO's, ψ_{n-1} and ψ_n, and the two LUMO's, ψ_{n+1} and ψ_{n+2}, using CI theory. The calculated electronic transitions are compared with those of the experimental data to verify the non-planar structure of the DQ molecule.

KEY WORDS: CNDO/SCF molecular orbital calculations, 4,4'-Dimethoxydiquinone, Uracil, Ionization potentials, Electron affinities

INTRODUCTION

The charge transfer ability values have been calculated for various pyridines and pyrimidines by CNDO/2 [1]. Charge transfer complex formation between nucleic acid bases and isoproternol has been demonstrated from UV absorption measurements [2]. UV absorption studies on weak interactions of adenine, cytosine, thymine and uracil with catechol in aqueous solutions containing 0.1 N HCl has given evidence for the formation of charge transfer complexes [3]. The regularities of the donor-acceptor interaction of nucleic acid bases and some of their derivatives with the strong acceptor 7,7,8,8-tetracyanoquinodimethane in thin amorphous films at 77 ^{o}K has been studied using UV and visible spectroscopy [4]. Lahir has studied charge transfer complex formation between, oxytetracycline and tetracycline, with purines, pyrimidines and amino acids [5]. A CNDO study of the tautomeric structure of uracil and its effect on the electrochemical corrosion behavior of mild steel in acid media has been performed [6].

The ionization potentials and the electron affinities for the possible tautomers of uracil have been calculated via the SCFMO method [7].

In the present work, the self-iterative eigenvectors were used to calculate the charge densities of the cations and the anions for the possible tautomers of uracil. The columbic energies of the donor and the acceptor were calculated and the structure of the DQ molecule was studied, in comparison with biphenyl, diquinone and methoxyquinone using CNDO calculations.

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EXPERIMENTAL

Uracil (Biochemical BDH) was obtained commercially and its purity was checked by measuring the melting point. DQ, 4,4'-dimethoxydiquinone, was prepared by Hammam [8] and recrystallized from dioxane as golden needles. This compound is sensitive to light therefore it should be kept in the dark. Absolute ethanol was used as a medium of the charge transfer studies. The electronic absorption spectra were recorded using Shimadzu UV-2101 PC UV-vis scanning spectrophotometer.

RESULTS AND DISCUSSION

CNDO calculations have been made as previously described for. rhenium-picric acid complex and some CNDO calculations in TNB, TNT and picric acid [9]. From our calculations for the planar and non-planar biphenyl molecule, it has been found that the hydrogen atoms in this molecule have positive charges (Tables 1, 2). From the CNDO calculations, the eigenfunctions have been used to calculate the total electronic energy in the ground state equilibrium geometries using the one-electron orbital energies ε_i in the total electronic energy ε as follows [9]:

$$\varepsilon_i = H_{ii} + \sum_j^n (2J_{ij} - K_{ij})$$

$$\varepsilon = 2\sum_i^n \varepsilon_i - \sum_i^n \sum_j^n (2 J_{ij} - K_{ij})$$

Table 1. CNDO Charge densities of the planar biphenyl molecule.

Atom	Charge	Atom	Charge
1 C	-0.0084	12 C	-0.0201
2 C	+0.0025	13 H	+0.0008
3 C	-0.0201	14 H	+0.0001
4 C	+0.0352	15 H	+0.0037
5 C	-0.0201	16 H	+0.0037
6 C	+0.0025	17 H	+0.0001
7 C	+0.0352	18 H	+0.0008
8 C	-0.0201	19 H	+0.0001
9C	+0.0025	20 H	+0.0037
10C	-0.0084	21 H	+0.0037
11C	+0.0025	22 H	+0.0001
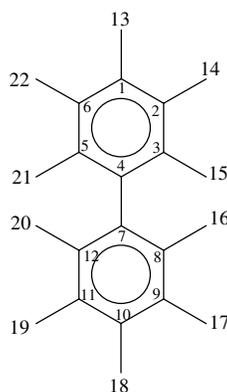
The energy difference between the equilibrium geometries of the planar and vertical biphenyl molecules for the total electronic energy is small, i.e. 0.0116 au (au = 27.2116 eV). Therefore the biphenyl molecule has conformers in which the planes of the two phenyls rotate against each other around the bond between the two phenyl moieties.

Extending our calculations to half of a DQ molecule, i.e. methoxyquinone, to reveal the effect of the presence of two oxygen atoms in the quinone moiety in addition to the methoxy group, it has been noticed from the charge densities for the vertical and planar forms (Tables 3,

4) that the negative charges on the oxygen atoms are on the expense of the charges of carbon atoms, with which the oxygen atoms are attached, and on the expense of the charges of hydrogen atoms attached with the ring. The positive charges of the carbon atoms attached with the oxygen atoms in the ring are not affected strongly in the vertical and planar forms. Also the negative charges at the carbon atoms in the ring are on the expense of the positive charges of the hydrogen atoms attached to the ring. Generally the charges of methoxyquinone are not affected strongly by changing the orientation of the methoxy group with respect to the quinone moiety. The calculated dipole moment of vertical methoxyquinone molecule has the value 1.79319 D and the planar form has the dipole moment value 2.40405 D. The electron affinities and the ionization potentials of this molecule in the two forms have the values 0.5062, (0.5069), 0.5220 and (05145) au for the vertical and (planar) forms, respectively. It is clear that the electron affinities and ionization potentials for this molecule are very slightly affected by changing the orientation of methoxy group with respect to the quinone moiety. From a general point of view the changing of the orientation of the methoxy group does not affect the electronic features of this molecule, i.e. charge densities, electron affinity and ionization potential.

Table 2. Charge densities of a vertical biphenyl molecule.

Atom	Charge	Atom	Charge
1 C	-0.0217	12 C	-0.0299
2 C	+0.0117	13 H	+0.0012
3 C	-0.0299	14 H	+0.0008
4 C	+0.0524	15 H	+0.0014
5 C	-0.0299	16 H	+0.0014
6 C	+0.0117	17 H	+0.0008
7 C	+0.0524	18 H	+0.0012
8 C	-0.0299	19 H	+0.0008
9 C	+0.0117	20 H	+0.0014
10 C	-0.0217	21 H	+0.0014
11 C	+0.0117	22 H	+0.0008
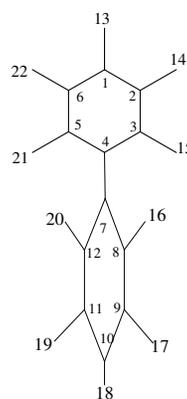
Table 3. Charge densities of planar methoxyquinone.

Atom	Charge	Atom	Charge
1 H_a	-0.0192	9 C	-0.0254
2 H_c	-0.0024	10 C	+0.2540
3 H_d	-0.0024	11 H	-0.1273
4 C_m	+0.1511	12 O	-0.2213
5 O	-0.1908	13 H	+0.0291
6 C	+0.1640	14 H	+0.0286
7 C	+0.2117	15 O	-0.2515
8 C	-0.0392	16H	+0.0410
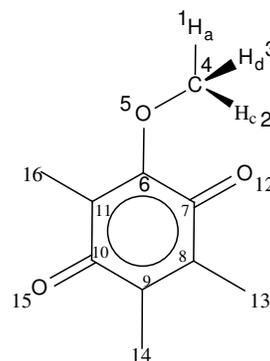
Table 4. Charge densities of vertical methoxyquinone.

| Atom	Charge	Atom	Charge
1 Ha	+0.0006	9 C	-0.0289
2 Hc	-0.0132	10 C	+0.2531
3 Hd	-0.0097	11 C	-0.1233
4 Cm	+0.1470	12 O	-0.2148
5 O	-0.2023	13 H	+0.0295
6 C	+0.1670	14 H	+0.0286
7 C	+0.2112	15 O	-0.2479
8 C	-0.0368	16 H	+0.0400
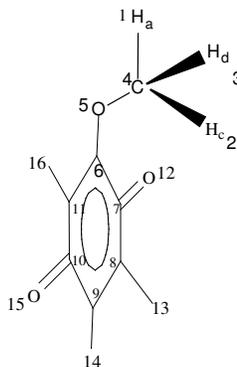
Planar diquinone molecule has a steric hindrance between the two oxygen atoms of the carbonyl groups and the opposite hydrogen atoms, in the two phenyl moieties therefore diquinone molecule has the more adequate non-planar structure. From comparative point of view, the charge densities of diquinone are similar to the methoxyquinone in the quinone moiety (see Table 5). The calculated dipole moment of vertical diquinone equals to 0.73039 D and the calculated electron affinity and ionization potential are equal to 0.4814 and 0.5101 au. Hence the DQ molecule has a vertical structure in which the planes of the two-phenyl groups are perpendicular. From the present previous studies it can be concluded that the electronic features of DQ molecule in the vertical form is similar to those of diquinone molecule and hence the DQ molecule is similar to the methoxyquinoe molecule in its electronic features.

Table 5. Charge densities of vertical diquinone molecule.

Atom	Charge	Atom	Charge
1 C	-0.0250	12 C	-0.0790
2 C	+0.2453	13 H	+0.0289
3 C	-0.0790	14 O	-0.2415
4 C	+0.0384	15 H	+0.0279
5 C	+0.2431	16 O	-0.2279
6 C	-0.0402	17 H	+0.0300
7 C	+0.0384	18 H	+0.0289
8 C	+0.2431	19 O	-0.2415
9 C	-0.0402	20 H	+0.0289
10 C	-0.0250	21 O	-0.2279
11 C	+0.2453	22 H	+0.0300
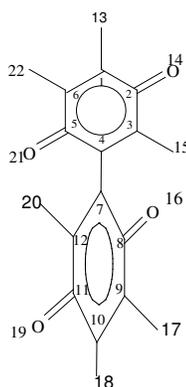
To study the charge transfer between uracil and the DQ molecule as if it were a planar molecule, the calculations have been based on the SCF-calculations since it has been concerned with the π-electron transfer as an approximation. It has been concluded that uracil has four possible tautomers [6]:
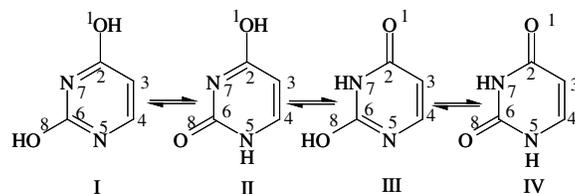
The possible tautomeric forms of uracil

The ionization potentials, I_D, of the HOMO's and the electron affinities of the LUMO's, E_A, for the possible uracil tautomers were calculated according to Pople [10] (Table 6).

$$E_m = \Sigma_u \, \Sigma_v \, C_{mu} \, C_{mv} \, F_{uv}$$

Table 6. The ionization potentials and the electron affinities of uracil tautomers and DQ molecule.

Compound	E_m eV	E_{m+1} eV
Uracil (I)	10.2066	0.8694
Uracil (II)	9.1765	2.1618
Uracil (III)	8.9872	2.0842
Uracil (IV)	10.3867	1.3331
DQ	9.1385	3.8416

Our SCFMO calculations [10-12] had been used to calculate the self-iterated eigenvectors of the self-iterated eigenvalues; hence the charge densities of the cationic and anionic forms of the studied molecules were calculated. The columbic potential energies of the molecular ions were calculated in addition to the columbic energy interaction in the CT-complex, taking into consideration that the dielectric constant of ethanol, is equal to 24.3 D. The distance [13] between the two molecular ions in the CT-complex is equal to 3.4 Å. The VSIP's, the bond resonance integrals and the one central repulsion integrals were taken from literature [14-16]. The bicentral repulsion integrals were calculated according to the Mataga equations [17].

According to the values of the ionization potential of the uracil tautomers I, II, III and IV with respect to that of the DQ molecule as if it were planar, they act as acceptors except tautomer III which acts as a donor since it has an ionization potential of, 8.9872 eV, which is lower than that of the DQ molecule, 9.1385 eV, while the electron affinity of the DQ molecule, 3.8416, is bigger than that of tautomer (III), 2.0842 eV. From the self-iterated eigenvectors of the self-iterated eigenvalues, the charge densities of the four possible tautomers of uracil as anion Z^-, acceptor, and cation Z^+, donor, were calculated (Table 7). Also the charge densities of DQ as if it were anion or cation when the DQ molecule acts as acceptor or donor, respectively, are given in Tables 8 and 9.

Table 7. The charge densities of uracil anions as acceptor and uracil (III) cation as donor.

Atom	Z^-(I)	Z^-(II)	Z^+(III)	Z^-(IV)
1 O	+0.0171	+0.0180	-0.0871	-0.4952
2 C	-0.1410	-0.1632	+0.1806	-0.0879
3 C	-0.0503	-0.0869	+0.2197	-0.1863
4 C	-0.2870	-0.1515	+0.1862	-0.2649
5 N	-0.2605	+0.0409	+0.0349	+0.0445
6 C	+0.0561	+0.0622	+0.3380	+0.2031
7 N	-0.3570	-0.2936	+0.0869	+0.0467
8 O	+0.0218	-0.4259	+0.0407	-0.2600

Table 8. Charge densities of DQ anion as acceptor.

Atom	Z^-	Atom	Z^-
1 O	+0.0215	10 C	-0.0523
2 C	+0.0270	11 C	+0.0270
3 C	+0.0917	12 C	+0.0917
4 C	-0.0921	13 C	-0.0921
5 C	-0.0387	14 O	+0.0215
6 C	+0.1136	15 O	-0.3029
7 C	-0.0523	16 O	-0.2678
8 C	-0.0387	17 O	-0.2678
9 C	+0.1136	18 O	-0.3029

Table 9. Charge densities of DQ cation as donor

Atom	Z^+	Atom	Z^+
1 O	+0.0231	10 C	-0.00957
2 C	+0.0641	11 C	+0.1450
3 C	+0.1450	12 C	+0.1450
4 C	+0.1972	13 C	+0.1972
5 C	+0.1175	14 O	+0.0231
6 C	+0.1473	15 O	-0.0658
7 C	-0.0096	16 O	-0.1186
8 C	+0.1175	17 O	-0.1186
9 C	+0.1473	18 O	-0.0659
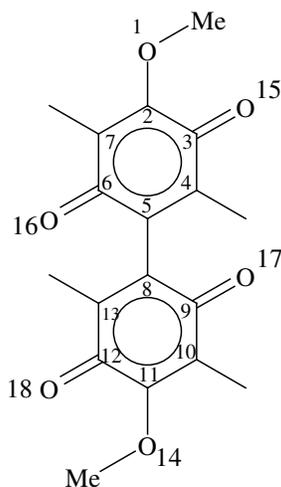
The solvation energies for the studied uracil tautomers have been calculated according to the following equation [18],

$$E_{solv} = -0.5(\Sigma_u\, q_u{}^2\, \gamma_{uu} + 2\Sigma_u\, \Sigma_v\, q_u\, q_v\, \gamma_{uv})\left(1 - (1/\varepsilon)\right)$$

where γ_{uu} = one central repulsion term, γ_{uv} = bicentral repulsion term, ε = the dielectric permitivity of ethanol, q_u = the charge density of a specific atom in the molecule studied.

The solvation energy of tautomer I has the lowest value, 1.6735 kcal mol^{-1} and tautomer IV has the highest one, 4.1079 kcal mol^{-1}. The solvation energies of the other tautomers, II and III, are adjacent, 2.9155 and 2.9656 kcal mol^{-1}, respectively.

The electron transfer energy in the CT-complex between the donor and the acceptor (cation and anion) was calculated according to the following equation [13].

$$E_{CT} = I_D - E_A - (C^+ + C^- + C^{+-})$$

where I_D is the ionization potential of the donor and E_A is the electron affinity of the acceptor.

C^+ is the columbic potential energy of the donor as a cation, and C^- is the columbic potential energy of the acceptor as an anion. C^{+-} is the columbic potential energy of the interaction between the anion of the acceptor and the cation of the donor in the CT-complex, regarding the dielectric constant of the solvent and the distance [13] between the molecular ions in the complex, 3.4 Å.

The columbic potential energy can be calculated, Table 10, according to the following equation [19],

$$C = \sum_{i=1}^{N} \sum_{j=1}^{N} Z_i \, Z_j / r_{ij}$$

where Z_i and Z_j are the charge densities and r_{ij} is the distance between two atoms in the molecule of N atoms.

From the values of the charge transfer energies, Table 11, the energy of the charge transfer between tautomers III and DQ molecule, 2.4793 eV (501 nm) is coincident accidentally with the experimental result, 500 nm, in ethanol. The band position in nm is obtained by dividing 1240.824 by the charge transfer energy in electron volts.
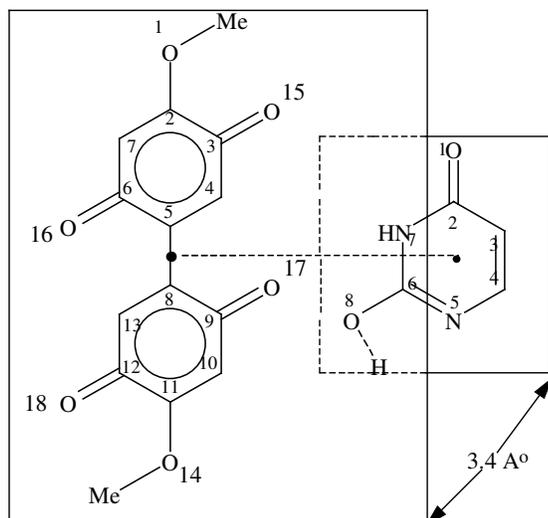
The suggested figure of CT-complex of uracil and DQ molecule; regarding the two centers of the two molecular ions are being coincident.

Table 10. The columbic potential energies and columbic potential energy of interaction for uracil-DQ complex in ethanol. Molecule to the left is donor and to the right is acceptor.

CT-com.	C^-, eV	C^+, eV	C^{+-}, eV
DQ-Ur (I)	2.3198	2.4797	-0.1458
DQ-Ur (II)	2.3198	1.7594	-0.1390
Ur (III)-DQ	2.7971	-0.0029	-0.1279
DQ-Ur (IV)	2.3198	1.2348	-0.1369

Table 11. The calculated charge transfer energies of DQ-Uracil complex in ethanol. Molecule to the left is donor and to the right is acceptor.

CT-com.	E^{CT} eV	E^{CT} nm	E^{CTexp} nm
DQ-Ur (I)	3.6155	343	-
DQ-Ur (II)	3.0365	409	-
Ur (III)-DQ	2.4793	501	500
DQ-Ur (IV)	4.8514	256	-

The configuration interaction calculations were carried out to compute the electronic transition energies for the singlet and triplet transitions between the highest two LUMO's and the lowest two LUMO's using the SCF calculations since we are dealing with π-electron transitions as an approximation. The coulomb-electron interaction integrals, J_{ab}, and the exchange electron interaction integrals, K_{ab}, have been calculated according to Nagy [20]. These calculations were carried out between the ground configurations, Φ_0, and the eight excited configurations, whose symbols are $^3\Phi_1$, $^3\Phi_2$, $^3\Phi_3$, $^3\Phi_4$, $^1\Phi_5$, $^1\Phi_6$, $^1\Phi_7$ and $^1\Phi_8$. From data in Tables 12 and 13, the electronic transitions calculated by CI theory [19] for uracil tautomer III and DQ molecule as a planar molecule do not contain absorption at 500 nm, verifying that the absorption band at 500 nm is due to the absorption of the charge transfer between uracil tautomer III and DQ molecule (see absorption band position in the Figures 1-3). Also the spectrum of DQ molecule does not contain the spectra of the planar molecule indicating the non-planar structure of the DQ molecule. Sure, the coincidence of calculated and the experimental charge transfer band position is accidental since the two-phenyl moieties in DQ molecule are non-planar.

Table 12. Calculated electronic absorption spectra of uracil tautomer III.

Transition	E eV	E nm	M_x	M_y	E_{exp} nm
$\Psi_g \dashrightarrow {}^3\Psi_{ex1}$	2.8161	441	0.4790	1.0490	----
$\Psi_g \dashrightarrow {}^3\Psi_{ex2}$	3.7597	330	0.4790	1.0490	----
$\Psi_g \dashrightarrow {}^3\Psi_{ex3}$	4.2697	291	-0.2890	0.8310	----
$\Psi_g \dashrightarrow {}^3\Psi_{ex4}$	5.0072	248	-0.2970	0.3300	255
$\Psi_g \dashrightarrow {}^1\Psi_{ex5}$	7.5012	165	-0.861	-0.361	----
$\Psi_g \dashrightarrow {}^1\Psi_{ex6}$	8.2944	150	-0.8590	0.8440	----
$\Psi_g \dashrightarrow {}^1\Psi_{ex7}$	8.5598	145	0.2590	-0.0030	----
$\Psi_g \dashrightarrow {}^1\Psi_{ex8}$	9.2881	134	0.2590	-0.0030	----

Table 13. Calculated electronic transitions of DQ molecule as if it were planar.

Transition	E eV	E nm	M_x	M_y	E_{exp} nm
$\Psi_g \dashrightarrow {}^3\Psi_{ex1}$	1.7189	722	0.8623	0.8176	----
$\Psi_g \dashrightarrow {}^3\Psi_{ex2}$	2.6112	475	0.7698	0.7592	----
$\Psi_g \dashrightarrow {}^3\Psi_{ex3}$	3.0840	402	0.000	0.000	----
$\Psi_g \dashrightarrow {}^3\Psi_{ex4}$	3.5510	349	0.000	0.000	365
$\Psi_g \dashrightarrow {}^1\Psi_{ex5}$	3.5800	347	0.000	0.000	----
$\Psi_g \dashrightarrow {}^1\Psi_{ex6}$	4.0660	305	0.000	0.000	----

	4.4659	278	2.0777	1.3076	274
$\Psi_g \ ----\blacktriangleright \ {}^1\Psi_{ex7}$					
$\Psi_g \ ----\blacktriangleright \ {}^1\Psi_{ex8}$	5.1988	239	2.1137	1.3424	----

Ψ_g is the state function of the ground state. Ψ_{ex} is the state function of the excited state. M_x is the transition moment component in the x-direction between the ground state and the excited state. M_y is the transition moment component in the y-direction between the ground state and the excited state.
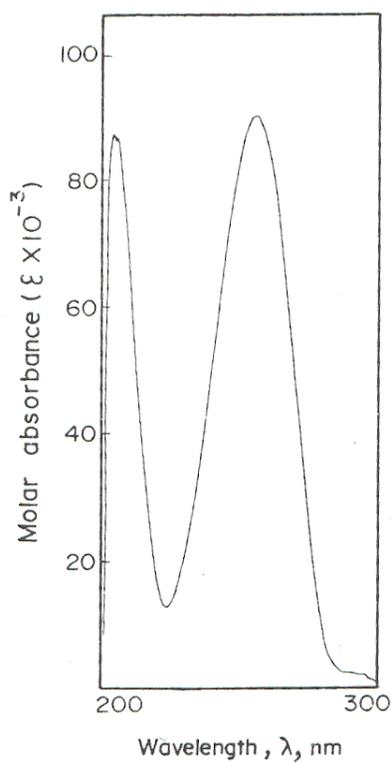

Figure 1. Electronic absorption spectrum of uracil in ethanol.
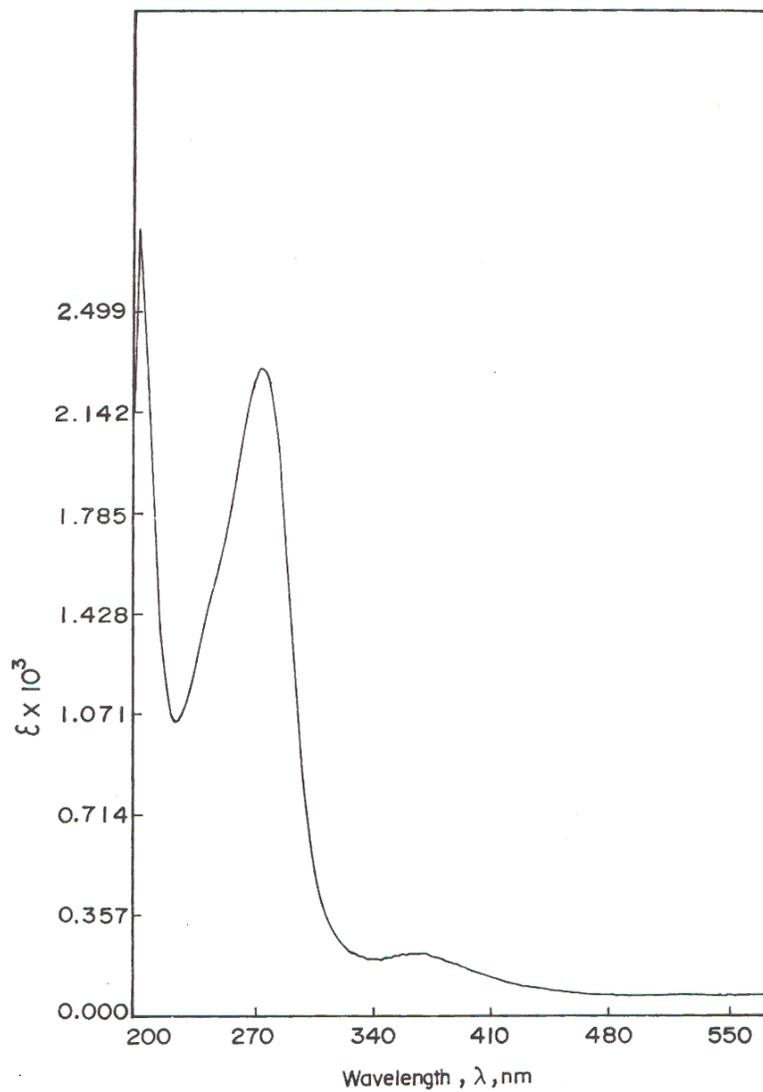
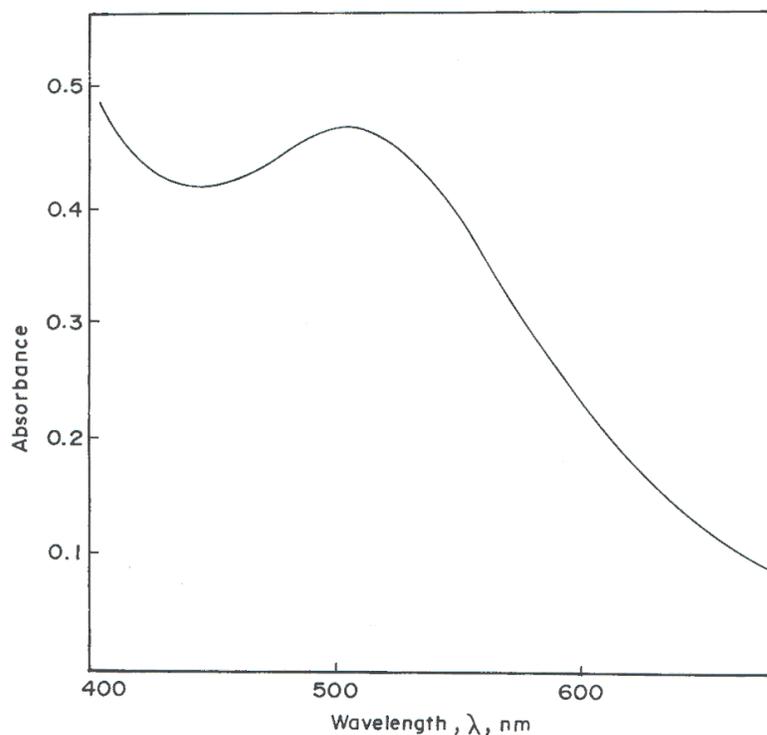Figure 2. Electronic absorption spectrum of DQ molecule in ethanol.

Figure 3. The charge transfer band of 1:1 uracil (III)-DQ complex in ethanol.

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