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RESEARCH ARTICLE

UV-vis, IR spectra and Computational studies of charge transfer complex formed between Benzochromene and π-Acceptors.

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Manuscript Info

Abstract

Three charge-transfer complexes formed between three π-acceptors (picric acid, chloranilic acid and 2,3 – dichloro - 1,4 - naphthquinone) with benzo-chromene as donor were synthesized and characterized by electronic, IR spectroscopy and elemental analysis. Elemental analysis and photometric titration of investigation demonstrate that the molar ratio of the synthesized charge transfer complexes as 1: 2 ratios (donor:acceptor). The spectroscopic and physical data were estimated using Benesi-Hildebrand and its modification method in terms of formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy $(\Delta G°)$, oscillator strength (f), ionization potential (I_P) and transition dipole moment (μ). Determination the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) reveal that charge transfer are within the molecule.

Introduction:-
Mullikan suggested that the formation of molecular complexes from two molecules can arise from a π-molecular orbital of a Lewis base to a vacant π-molecular orbital of a Lewis acid with resonance between the dative structure and no bond structure stabilizing the complex. He also suggested the possibility of a complex formation through donating of an electron from a non-bonding molecular orbital in a Lewis base to a vacant π-orbital of an acceptor $(n \rightarrow \pi^*)$ interaction with resonance stabilization of the combination (Mulliken, 1950; 1952; 1952). Many compounds like multirings aromatic hydrocarbons, aromatic amines form charge transfer complex with many acceptors (Srivastave et et al., 1966; 1970; Dwinedi et al.,1983). Charge transfer interactions formed between perhydroisoquinoline as donor with 2,6-dichloroquinone-4-chloroimide, 2,6-dicbromoquinone-4-chloroimide, chloranilic acid and picric acid as acceptors have been studied spectrophotmetrically (Refat et al., 2008). Conductometric study for formation of charge transfer complexes, revealed that the stoichiometry of naphthalene-picric acid complex as 1:1 and that of the biphenyl-picric acid and p-phenylende-diamine: p-chloranil complexes as 2:1 (Ramanamurti et al.,1982). A spectrophotometeric method is developed for the quantitative determination of some primary aliphatic and aromatic amines, based on the interaction between these amines and 2,4-dinitrofluorobenzene (Al-Sabha et al.,2015). The spectrophotometric characteristics of the solid charge-transfer molecular complexes (CT) formed in the reaction of the electron donor 2-amino-6-ethylpyridine with the π-acceptors have been studied. The results show that the formed solid CT complexes have ratio 1:2 with tetracyanoethylene and 2:1 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Mostafa et al., 2014). Energy minimization is an important step in molecular modeling with applications in molecular docking and in mapping binding sites. Charge transfer complexes of substituted aryl Schiff bases as donors with picric acid and m-dinitrobenzene as acceptors were investigated by using computational analysis calculated (Al-Harbi et al.,2014). The reaction of 2,3-dichloro-1,4-naphthoquinone with crizotinib was investigated, the stoichiometric ratio was found to be 2:1. Computational molecular modeling for the complex was conducted and the mechanism of the reaction was postulated (Alzoman et al., 2015). Spectroscopic and computational studies on the CT complex of 1,10-

phenanthroline and picric acid have been studied with a view to know the type and nature of interaction between them (Srivastavaa et al., 2015).

In this work, we synthesize some new charge transfer complexes of benzochromene (BC) as an electron donor with picric acid (PA), chloranilic acid (CLA) and 2,3-dichloro-1,4-naphthquinone (DNQ) as π-acceptors (Formula 1). UV-V and IR spectroscopic studies of compounds are used to deduce the structure and new electrical behavior of these new compounds. Calculations of the formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy $(\Delta G°)$, oscillator strength (f) and transition dipole moment (μ) also the HOMO-LUMO energy gap of the molecules have been done.
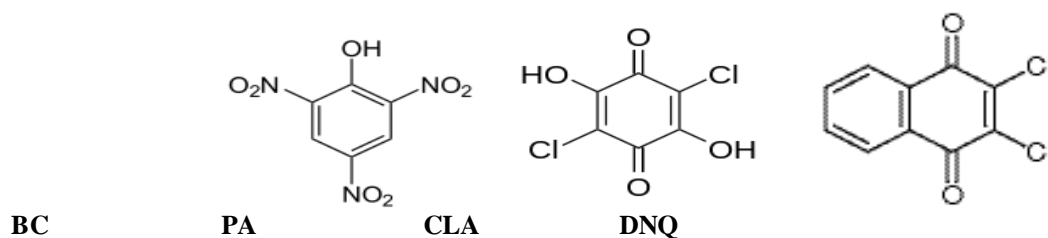
Formula 1. Structure of donor and π-acceptors.

Experimental:-
1. Materials:-
All chemicals used were of analytical grade. Benzochromene was prepared as reported else where (Barsy et al., 2015) and purity of the obtained product was checked by melting point and elemental analysis measurements [$C_{22}H_{19}NO_3$; Mol.wt. =345.398; white; M.p.= 220 °C; Calc.: % C 44.53, % H 2.39; Found: % C 42.99, % H 2.89]. Picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthquinone were purchased from Sigma.

2. Physical measurements:-
The electronic absorption spectra were recorded in the region of 800–200 nm by using a Perkin-Elmer Lambda 25 spectrophotometer with a 1 cm quartz cell. The mid infrared spectra (IR) measurements of the solid CT-complexes as KBr discs were carried out on a Genesis II FTIR spectrophotometer in the range of 4000–400 cm^{-1}. Melting point was measured on Gallenkamp melting point apparatus and is uncorrected. The data of the elemental analyses of the newly synthesized CT-complexes are consistence with the molar ratio results obtained from the photometric titrations.

3. Photometric titrations:-
The reported photometric titrations were performed at different wavelengths namely 351, 294 and 408 nm for the complex derived from benzochromene and picric acid (complex **I**), chloranilic acid (complex **II**) and 2,3-dichloro-1,4-naphthquinone (complex **III**) respectively. A 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 or 3.00 ml aliquot of a standard solution (5.0 × 10^{-4} mol/L) of the appropriate acceptors in methanol was added to 1.00 ml of 5.0×10^{-4} mol/L of donor also in methanol. The total volume of the mixture was been made up to 5 ml. The concentration of donor (C_D) in the reaction mixture was thus fixed at 1.0×10^{-4} mol/L while the concentration of π-acceptors (C_A) varied from 0.25×10^{-4} to 3.00×10^{-4} mol/L. These concentrations produce donor: acceptor ratios from 4:1 to 1:4. The absorbance of each CT complexes was measured and plotted as a function with the ratio of $(C_D):(C_A)$ according to a known method (Skoog,1985). Modified Benesi–Hildebrand plots were constructed to allow the calculation of the formation constant, K_{CT}, and the molar extinction coefficient, ε_{CT}, values for each CT complex in this work (El-Kourashy, 1981).

4. Syntheses Solid Charge Transfer Complexes:-
The solid CT-complexes were prepared by mixing 1 mmole of the Benzochromene in methanol (20 ml) with 2 mmole of picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthquinone in the same solvent (10 ml). The mixtures were stirred at room temperature for 3 h then left over night to separate the solid complex I, II and III respectively which were filtered off, washed several times with little amounts of methanol, and then dried under vacuum over anhydrous calcium chloride (Formula 2). The complexes were characterized using spectroscopic techniques (IR and UV-vis) and elemental analysis in addition to some physical properties and the results are summarized as follows:
Complex **I**: $C_{34}H_{25}N_7O_{17}$; Calc.: % C = 50.842; % H = 3.137; Found: % C = 50.99; % H = 3.79; Mol.wt. = 803.33; M.p.= 285°C; yellow.

Complex **II**: $C_{34}H_{23}NCl_4O_{11}$; Calc.: %C=53.52; %H=3.04; Found: %C = 53.37; %H, 3.09; Mol. wt.= 762.98; M.p.=290 $^{\circ}$C; Dark brown.

Complex **III**: $C_{42}H_{27}NCl_4O_7$; Calc.: % C = 63.13; % H = 3.41; Found: % C = 63.71; %H = 3.12; Mol.wt.=799.10; M.p. = 270 $^{\circ}$C; yellow.

5. Computational studies:-

The drawing of the structure of the donor and acceptors were carried out on the Chem. Draw ultra 12.0 software and for optimization the obtained structures were transported to program Chem. 3D ultra 12.0.

Formula 2. Charge transfer complex of Benzochromene (BC) with picric acid (PA), chloranilic acid (CLA) and 2,3-dichloro-1,4-naphthquinone (DNQ).

Results and Discussion:-

1. Infrared Spectra:-

The peak assignments for the important characteristic IR spectral bands for the formed CT complexes are shown in Figure 1 and Table 1. A comparison of the relevant IR spectral bands of the free benzochromene (BC) and the studied acceptors (PA, CLA and DNQ) with the corresponding bands in the IR spectra of the isolated solid CT complexes clearly indicated that the characteristic bands of the BC exhibit small shifts in frequency and changes in their band intensities (νOH, νNH_2 at 3403-2903 cm^{-1} and $\nu C=O$ at 1525 cm^{-1}). This result could be attributed to the expected changes in symmetry and electronic configurations upon the formation of the CT complexes.

The $\nu(OH)$ stretching vibrations in the free PA and CLA appeared at 3416, 3235 cm^{-1}, respectively, where in the formed CT complexes, these stretching vibrations occurred at 3430 cm^{-1} for complex **I**; at 3481 cm^{-1} for complex **II**.

The IR spectrum of the complexes **I**, **II** are characterized by appearing of band at 3032, 3232 cm^{-1} which does not appear in the spectra of the free donor or PA and CLA. This band can be attributed to the stretching vibration of the intermolecular hydrogen bond (OH---N) in the complex formed through the transfer of a proton from the acidic center of PA and CLA to the donor as dictated by acid–base theory (Adam, 2012; 2013). The shift of the IR bands of the acceptor to lower wavenumbers reflects a donor to acceptor charge transfer of n → π* interaction, $D_{HOMO} \rightarrow D_{LUMO}$ transition (Formula 2) (Bharathikannan et al., 2008).

In the complex **III**, the stretching vibration of $\nu(C=O)$ appear at 1621 cm^{-1} was shifted to a lower value 1587 cm^{-1}, that is indicative of the involvement of the (C=O) group in the CT-complexation. The π→π* CT complex **III** is formed via the benzochromene (electron-rich group) and the DNQ (electron acceptor). The chloro- and C=O are an electron withdrawing groups that exists in DNQ. The chloro and C=O groups in DNQ withdraw electrons from the aromatic ring and such a process will make the aromatic ring an electron accepting region (Formula 2). It might also to indicate here that $\upsilon(NO_2)$ vibrations of PA show some changes particularly in terms of band wavenumber values from 1861 to 1813 cm^{-1} upon complexation. The stretching vibration of $\nu(C-Cl)$ appears at 981 and 851 cm^{-1} for CLA; at 889 and 838 cm^{-1} for DNQ. This band is observed at a range of 823-978 cm^{-1} for the CT complexes **II** and **III**.
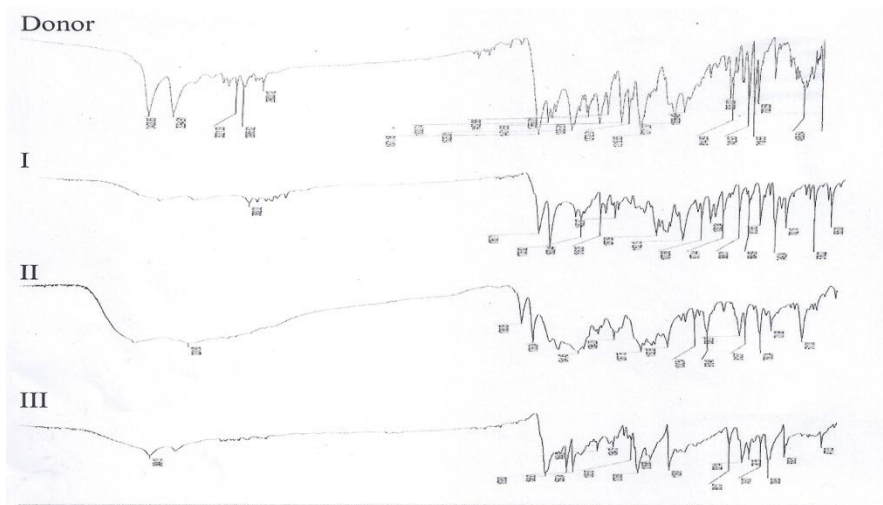
Fig. 1. IR data for donor, I, II and III CT-complexes.

Formula 2. Suggested structure of **I** [BC(PA)$_2$], **II** [BC(CLA)$_2$] and **III** [BC(DNQ)$_2$] complexes.

Table 1. Electronic (nm), IR (cm^{-1}) data for the new CT complexes.

Compound	λ_{max} nm	v O-H + υN-H	OH---N	υC=O
Complex **I** [BC(PA)$_2$]	210, 216, 225, 234, 355	3485, 3352	3032	
Complex **II** [BC(CLA)$_2$]	228, 254, 275, 302, 307, 311, 524	3485	3232	1541
Complex **III** [BC(DNQ)$_2$]	214, 220, 230, 236, 240, 244, 260, 288, 336	3404	-	1587

2. Electronic absorption spectra:-

The electronic absorption spectra of the Benzochromene, π-acceptors and the resultant charge transfer complexes are shown in Fig. 2. The spectra revealed new strong absorption bands assigned to the CT interaction at 355, 524 and 336 nm for I, II and III complexes, respectively (Table 1). The photometric titration (Skoog, 1985) measurements between benzochromene and CLA, DNQ and PA in methanol based on the characteristic absorption bands with reference to the CT-complexes (Fig. 3), proved that the molar ratio of the resultant complexes is 1:2 donor:acceptor (Fig. 4). It was necessary to calculate the values of the formation constant (K$_{CT}$) and the extinction coefficient (ε_{CT}) of the complexes. For this purpose, the 1:2 modified Benesi–Hildebrand equation was used in the calculations (El-Kourashy, 1981):

$$(Ca)^2 C_d/A = 1/K_{CT}\varepsilon_{CT} + 1/\varepsilon_{CT} C_a (4C_d + C_a)$$

where C$_a$ and C$_d$ are the initial concentration of the acceptors and donor, respectively and A is the absorbance of the detected CT band. The data obtained C$_a$, C$_d$, $(Ca)^2 C_d$, $C_a(4C_d+C_a)$ and $(Ca)^2 C_d/A$ were calculated. By plotting $(Ca)^2 C_d/A$ values vs. $C_a(4C_d+C_a)$, straight lines are obtained with a slope of $1/\varepsilon_{CT}$ and an intercept of $1/K_{CT}\varepsilon_{CT}$.

The values of both K_{CT} and ε_{CT} associated with these complexes are given in Table 2. The data resulted (Table 2) show that the complexes give high values of both formation constant (K_{CT}) and molar extinction coefficient (ε_{CT}). The high values of both K_{CT} and ε_{CT} of the resultant CT-complexes caused high stabilities of the formed CT-complexes to be expected as a result of the expected high donation of the benzochromene.
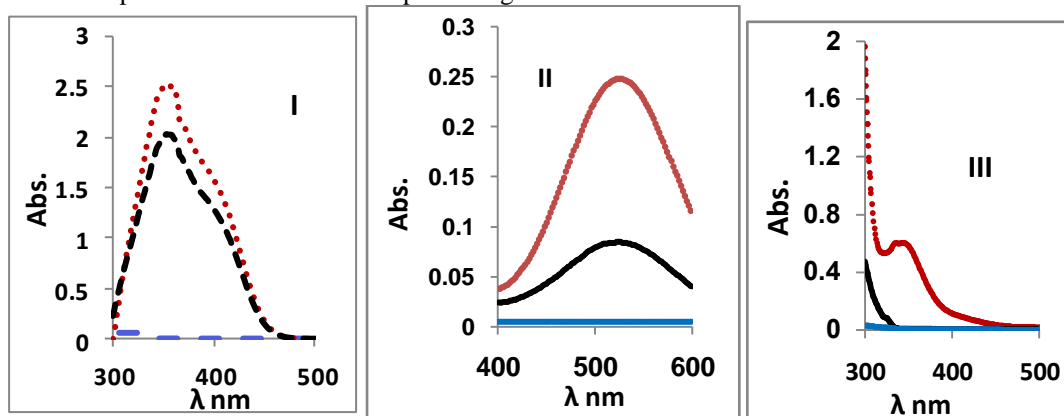

Fig. 2. Electronic absorption spectra of the donor, acceptors and of the CT-complexes **I**, **II** and **III**. The blue color is for the donor and the black color is for the acceptors while the orange color is for the CT complexes.
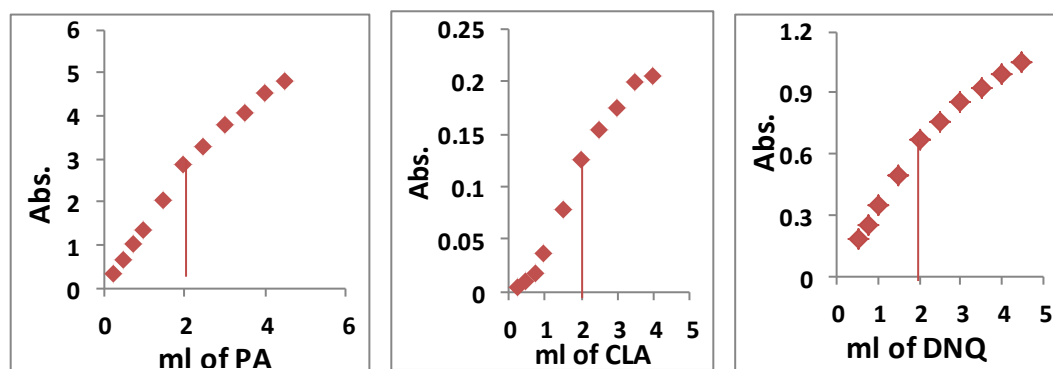
Fig.3. Photometric titration curves of picric acid, chloranilic acid and 2,3dichloro-1,4-naphthquinone with benzochromene.
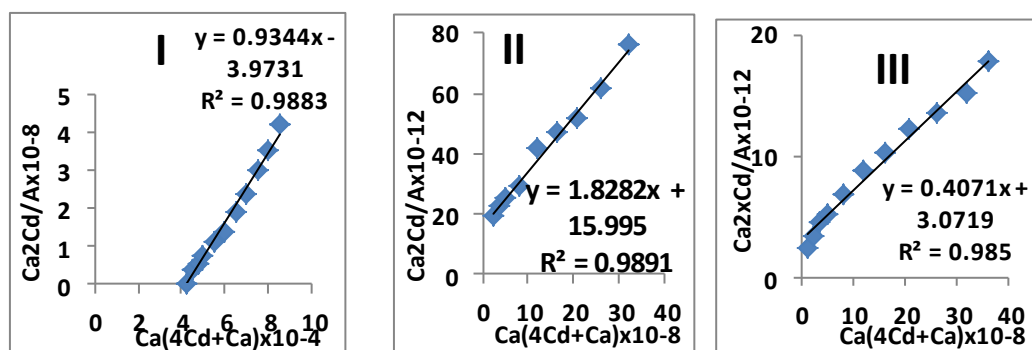

Fig.4. The plot of Ca(4Cd + Ca) values against $(Ca)^2Cd/A$ values of **I**, **II** and **III** complexes.

3. Physicochemical parameters for the charge transfer complexes:-

In order to characterize the formation of the complexes between BC and the acceptors, some physicochemical parameters were estimated to explain the propensity of the formation of the complexes. The oscillator strength (f) is a dimensionless quantity used to express the transition probability of the CT band. The oscillator strength (f) was obtained from the approximate formula (Tsubomura et al.,1964):

$$f = 4.319 \times 10^{-9} \varepsilon_{CT} \nu_{½}$$

The transition dipole moment (μ) of the CT complex calculated from equation (Rathore et al., 1997):

$$\mu(Debye) = 0.0958 [\varepsilon_{CT} \nu_{\frac{1}{2}} / \nu_{CT}]^{1/2}$$

where $\Delta\nu_{1/2}$ is the half-width, that is the width of the band at the half the maximum absorption, and $\Delta\nu$ $\approx$ wavenumber at the absorption maximum.

The resonance energy of the complex (R_N) in the ground state is obtained from the theoretical equation derived by Brieglab (Briegleb et al., 1960):

$$\varepsilon_{CT} = 7.7 \times 10^{-4} / [h\nu_{CT} / [R_N] - 3.5]$$

where ε_{CT} is the molar absorptivity of the complex at the maximum of the CT absorption, $h\nu_{CT}$ is the transition energy of the complex.

The transition energy (E_{CT}) of the complex which is obtained from the expression (Briegleb et al.,1964):

$$E_{CT} = h\nu_{CT} = 1243.667 / \lambda_{CT} (nm)$$

where h is Planck's constant, ν_{CT} is the wavenumber of the absorption peak of the CT complex and λ_{CT} is the wavelength of the characteristic complexation band. The calculated spectroscopic and physical values (f, μ, R_N and E_{CT}) for the CT complexes using these equations are presented in Table 2.

It has been accounted the values of electronic transitions energies (E_{CT}) for complexes according to the following equations:

$$E_{CT} = h\nu_{CT} \text{ (eV)} = 1243.667 / \lambda_{CT} (nm)$$
$$h\nu_{CT} \text{ (KJ mol}^{-1}) = h\nu_{CT} \text{ (eV)} \times 96.49$$
$$h\nu_{CT} \text{ (cm}^{-1}) = h\nu_{CT} \text{ (eV)} \times 8066$$

The value of transition energy of the complexes was 228.971-357.147 KJ mol^{-1} and 19140.618-29855.411 cm^{-1} for complex **I**, **II** and **III** respectively.

The ionization potentials (Ip) of the electron donor can be obtained from charge transfer absorption bands by using different methods.

The ionization potential of the donor in the charge transfer complex is calculated using the empirical equation derived by Aloisi and Pigantro (Aloisi et al., 1972).

$$Ip_{(eV)} = 5.76 + 1.53 \times 10^{-4} \nu_{CT}$$

From the above equation, the value of ionization potential of donor with picric acid in CT of complex I = 10.08 (eV).

The ionization potential of an unknown donor can be obtained from the $h\nu_{CT}$ vs Ip plot (Ghosh et al.,1993) for PA with a number of other donors, hexol (Refat et al., 2013), p-nitroaniline (Singh et al., 2009), ibuprofen (Sultana et al., 2013), N-dimethylbenzylidene aniline (Gaber et al., 1988). Evaluated Ip values of benzochromene are shown in the inset, provided the value of ν_{CT} for the unknown donor is known for the same acceptor, the value of Ip obtained from this plot for donor =10.1 eV (figure 5). The charge-transfer band energy can be approximately related to the ionization potential of the donor and electron affinity of the acceptor molecule given by equation (Foster et al., 1966).

$$h\nu_{CT} = Ip - E_A - W$$

where h is the Planck's constant, ν_{CT} is the frequency corresponding to the lowest energy intermolecular charge-transfer band, Ip is the ionization potential of the donor, E_A is the electron affinity of the acceptor and W a constant.

Again assuming that the dissociation energy W values are essentially constant for similar type of complexes, the relationship between the ionization potential of two donors and the values of ν_{CT} with a common acceptor (PA) can be written as:

Ip donor (2) = Ip donor (1) + $h\nu_{CT}$ (2) - $h\nu_{CT}$ (1).

From the above, the value of ionization potential of donor (2) can be estimated if the ionization potential of donor (l) and the associated values of ν_{CT} are known. Assuming Ip for 4 - (2 - aminoethyl) phenol - picric acid complex = 9.64 eV and ν_{CT} = 3.16 eV (AbuYamin et al., 2013), we have estimated the value of ionization potential of donor = 9.993(eV). The average value of ionization potential of donor estimated by three different methods =10.058 (eV). There is a little difference between the three sets of values.

In Table 2, the values of ionization potential of donor in CT complexes **I**, **II** and **III** by using equation derived by Aloisi and Pigantro. The dissociation energy (W) of the formed CT complex between donor and acceptors was calculated from the transition energy ($h\nu_{CT}$), ionization potential of the donor (Ip) and the electron affinity of picric acid ($E_A = 1.1$). The dissociation energy was found to be 2.651 (eV).
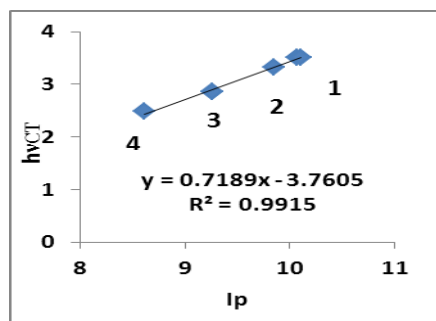
Fig. 5. Plot of $h\nu_{CT}$ against Ip for CT complexes of picric acid with 1-hexol, 2-p-nitroaniline, 3-Ibuprofen and 4-N-dimethylbenzylidene aniline.

Table 2. Physicochemical parameters of the CT complexes

Complex	λ_{CT} nm	K_{CT} Lmol^{-1}	ε_{CT} Lmol^{-1}cm^{-1}	F	μ	R_N	I_p eV	ΔG KJ mol^{-1}	E_{CT} eV
I [BC(PA)$_2$]	354	2.351x10^6	10.702x10^3	4.970	19.363	0.363	10.08	36.346	3.513
II [BC(CLA)$_2$]	524	12.784 x10^6	5.470 x10^3	1.552	13.635	0.119	8.680	40.542	2.373
III [BC(DNQ)$_2$]	336	13.252 x10^6	24.563x10^3	21.494	40.017	0.857	10.314	47.884	3.701

4. Molecular Modeling and energy gap:-

For investigating the site of interaction and postulate the reaction mechanism, modeling for the CT complex was performed. It was found that the highest electron density in the benzochromene molecule is located on the nitrogen atom of the amino group. The total charge on the nitrogen atom was found to be -0.103, the negative sign indicate the negative electron density. As well, it was found that acceptors moves toward the NH_2 group of donor to form the CT complex (Figure 6). In the NH_2 group, nitrogen can donate a major share of the lone pair of electrons to the oxygen atom of picric acid and chloranilic acid. This leads to the development of partial negative charges on the oxygen atom and this makes them capable of forming the charge transfer complex. Other centers did not contribute in the CT reaction based on the fact that certain electron density was required for achievement of a successful electron transfer (Foster, 1969).
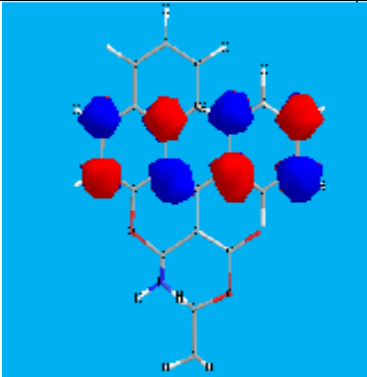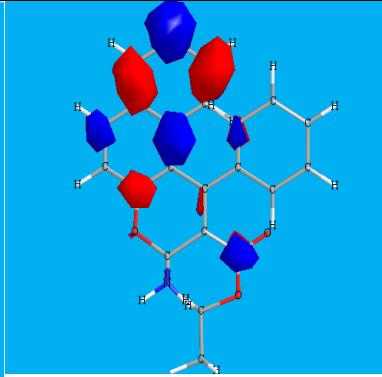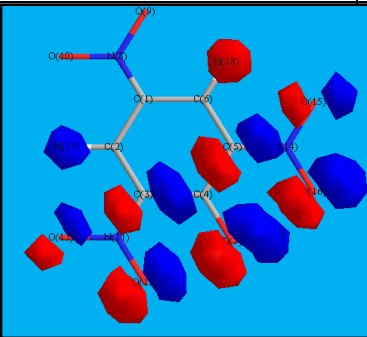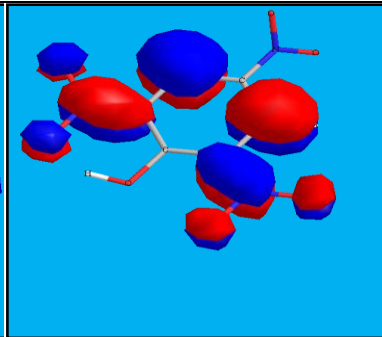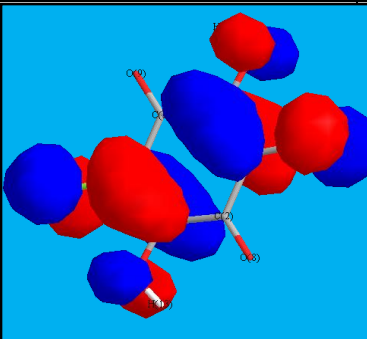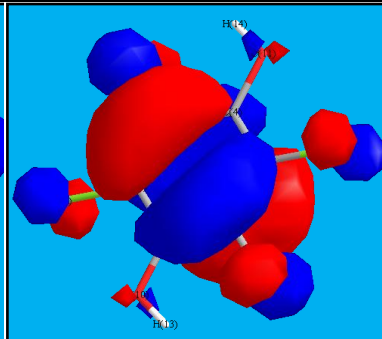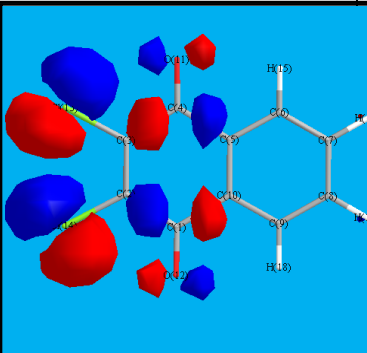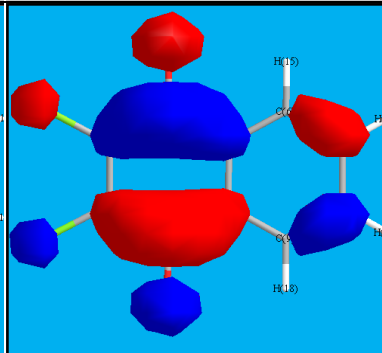
The HOMO-LUMO energy gap of donor, acceptors and CT complexes were calculated (Table 3). It is known that the value of E_{HOMO} is often associated with the electron donating ability of inhibitor molecule, higher values of E_{HOMO} is an indication of the greater ease of donating electrons to the unoccupied orbital of the acceptor. The value of E_{LUMO} is related to the ability of the molecule to accept electrons, lower values of E_{LUMO} shows the acceptor would accept electrons. Consequently, the value of Egap provides a measure for the stability of the formed complex.
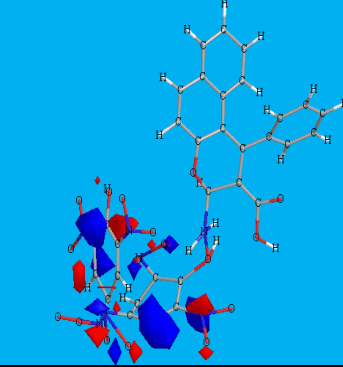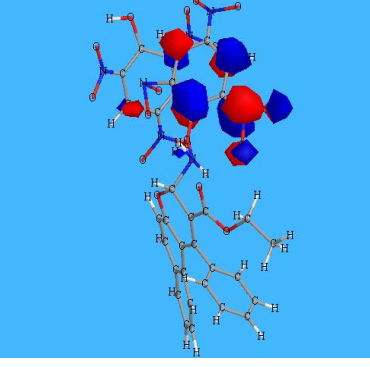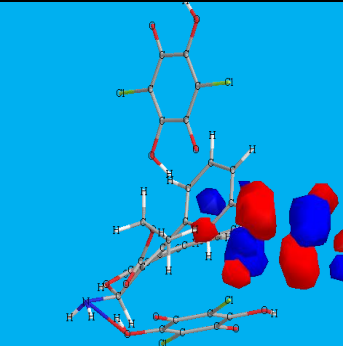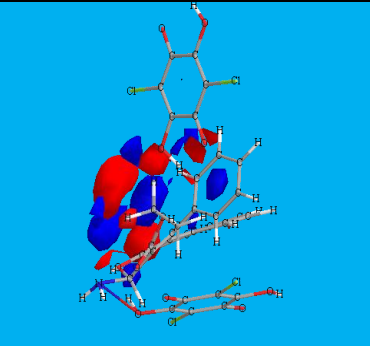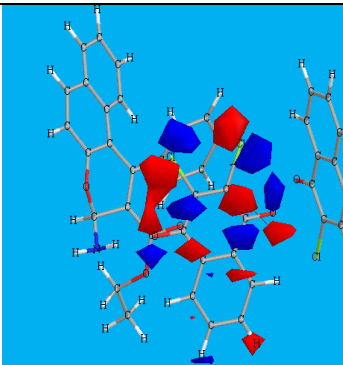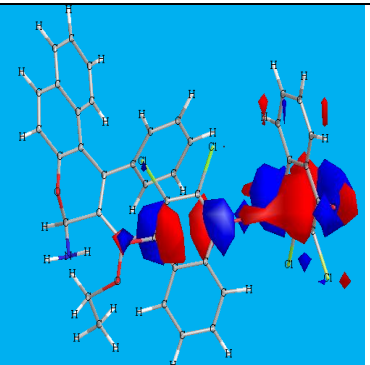
The order of stability can be summarized as: **I** > **II** > **III**. In the Fig. 6, show that acceptors are perpendicular to the molecular plane of donor. The optimized bond length, bond angle and dihedral angles of complexes which are calculated.

Table 3: The HOMO-LUMO energy gap of donor, acceptors and CT complexes in **eV.**

Compound	HOMO	LUMO	Energy gap
Benzochromene (BC)	0.236	1.530	-1.294
Picric acid (PA)	-11.290	-6.221	-5.069
Chloranilic acid (CLA)	-8.885	-7.326	1.559
2,3-dichloro-1,4-naphthquinone (DNQ)	-9.697	-7.195	-2.502
Complex I [BC(PA)$_2$]	-6.523	-5.580	-0.943
complex II [BC(CLA)$_2$]	-8.021	-6.935	-1.086
complex III [BC(DNQ)$_2$]	-9.956	-7.997	-1.959

Fig 6. Picture of HOMO-LUMO of donor, acceptors and CT complexes.

	HOMO	LUMO
Benzochromene (BC)		
Picric acid (PA)		
Chloranilic acid (CLA)		
2,3-dichloro-1,4-naphthquinone (DNQ)		

Complex I [BC(PA)₂]		
Complex II [BC(CLA)₂]		
Complex III [BC(DNQ)₂]		

Conclusions:-

The CT reaction of benzochromene as electron donor and picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthquinone as electron acceptors has been investigated. The obtained complexes were studied by spectrophotometric method. The formation constant (K_{CT}), the molar extinction coefficient (ε_{CT}) and physicochemical parameters (f, μ, R_N, I_p, ΔG and E_{CT}) for the CT complexes were calculated. The HOMO-LUMO energy gap of the donor, acceptors and CT complexes has been obtained.

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