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RESEARCH ARTICLE

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Synthesis, spectroscopic, and computational studies of charge-transfer complexation between benzidine with 2,3-dichloro-5,6-dicyano-p-benzoquinone and chloronil

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The solid charge transfer (CT) complexes that have been formed from the reactions of donor benzidine (BZ) and the π-acceptors such as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and chloronil (CHL) have been studied and characterized experimentally and theoretically. The experimental work which includes the use of UV-visible spectroscopy to identify the CT band of the CT-complex. The composition of the complexes has been investigated successfully by using spectrophotometric titration and Job method of continuous variation to be 1:1. Furthermore, to calculate the formation constant and molar extinction coefficient, we have used the Benesi-Hildebrand equation. Infrared and proton nuclear magnetic resonance spectral studies were used to characterize and confirm the formation of CT-complex. The experimental studies were well supported by quantum chemical simulations by using density functional theory. The computational analysis of molecular geometry, Mulliken charges, and molecular electrostatic potential surfaces of reactants and complexes is very much helpful in assigning the CT route. The C═O bond length of DDQ and CHL increased upon complexation with BZ. We have also observed that the substantial amount of charge has been transferred from BZ to DDQ and CHL in the process of complexation. An excellent consistency has been achieved between experimental and theoretical results.

KEYWORDS
benzidine, charge transfer complexes, DFT studies, electronic absorption spectra, molecular electrostatic potential

1 | INTRODUCTION

In principle, the charge transfer (CT) interactions are formed between the electron donors and the electron acceptors, which involves a resonance with a transfer of charge from the donor molecule to the acceptor molecule.[1–3] The formation of CT-complex is based on the interaction of the highest occupied molecular orbital (HOMO) of the donor with the lowest unoccupied molecular orbital (LUMO) of the acceptor. In general, the CT complexation occurs as an ionic band in a simple ion-radical pair interaction.[4]

Molecular CT materials have been paying great attention because of their attractive and realistic targets in materials science. The formation of molecular CT systems accompanied by the changes in magnetic, dielectric properties, and structural changes. These CT complexes not only exhibit fascinating optical, electrical, and photoelectrical properties but also play a vital role in many electrophysical and optical processes.[5] The CT complexation has acquired much importance in biochemical and bioelectrochemical energy transfer processes[6], biological systems[7], drug receptor, binding mechanism, drug action, enzyme catalysis, ion transfers

through lipophilic membranes,[8] etc. Certain electron donors and π-acceptors have been successfully used in the preparations of drug molecules in pharmaceutical industry.[9,10]

Although several electron donors have been used widely in pharmaceutical as well as in material science research field, the benzidine (BZ; 4,4'-diaminobiphenyl) and its derivatives are being used extensively in the production of dyes. Moreover, by using the BZ test, the presence of blood/haemoglobin in urine (haematuria) can be detected.[11] The haeme moiety of the haemoglobin has peroxidase-like activity that brings about the decomposition of hydrogen peroxide to liberate the nascent oxygen. The peroxidase activity of hemoglobin catalyzes the oxidation of BZ to form an intense blue color charge-transfer complex. Thus, the BZ is an important compound since it forms CT complex in the biological system. The electron-donating nature of the BZ can be explored in combination with the electron acceptors. From these perspectives, it is necessary to further investigate the properties of the CT complexes that are formed from the BZ. On the other hand, the electron acceptors such as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and chloronil (CHL) are most widely used in chemical synthesis for various applications.

The main objective of our work is to investigate the electron-donating strength of BZ by studying its CT complexes that are formed with DDQ and CHL, which are structurally similar but differs in their ionization potentials (IPs). In particular, isolation and spectral characterization of CT complexes were conducted in detail.

2 | EXPERIMENTAL

2.1 | Materials and stock solutions

All chemicals used in this study were of analytical grade. Benzidine, DDQ, and CHL were purchased from Avra chemicals whereas the acetonitrile and methanol were purchased from Sigma-Aldrich.

2.2 | Instrumentation and physical measurements

The electronic absorption spectra of the donor, acceptors, and the resulted CT complexes were recorded in the region of 350 to 700 nm by using a Shimadzu double beam spectrophotometer with a 1 cm quartz cell. The infrared (IR) spectral measurements (KBr discs) of the solid CT complexes were conducted on Fourier transform IR spectrophotometer in the 4000 to 250 cm^{-1} range. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Bruker DRX-250 spectrometer. The measurements were conducted at ambient temperature using dimethyl sulfoxide (DMSO) as the solvent and tetramethylsilane as an internal reference. ^{1}H NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in DMSO solvent.

2.3 | Synthesis and elemental analysis

Two solid CT complexes were synthesized from BZ with DDQ and BZ with CHL by mixing 1 mmol BZ with 1 mmol of each acceptor in methanol (10 ml). The reaction mixture was continuously stirred at room temperature for 20 minutes, which resulted in the precipitation of the solid CTC_1 (BZ-DDQ) and CTC_2 (BZ-CHL) complexes. The solid precipitates were filtered, washed several times with methanol. Finally, the solvent was removed and dried under vacuum over anhydrous calcium chloride. The data of the elemental analyses are as follows: CTC_1-mol formula = $C_{20}H_{12}Cl_2N_4O_2$. Elemental analysis = C, 58.41; H, 2.94; Cl, 17.24; N, 13.62; O, 7.78. m/z = 410.03 (100.0%), 412.03 (63.9%), 411.04 (21.6%), 413.03 (13.8%), 414.03 (10.2%), 412.04 (2.2%), 415.03 (2.2%), 411.03 (1.5%), 414.04 (1.4%). Lipinski rule = 410.034; 6; 2; 3; 0. CTC_2- mol formula = $C_{18}H_{12}Cl_4N_2O_2$. Elemental analysis = C, 50.27; H, 2.81; Cl, 32.97; N, 6.51; O, 7.44. m/z = 427.97 (100.0%), 429.96 (63.9%), 429.96 (63.9%), 431.96 (51.1%), 430.97 (24.9%), 428.97 (19.5%), 433.96 (13.1%), 432.96 (11.9%), 431.96 (10.2%), 431.97 (2.3%), 429.97 (1.8%), 434.96 (1.3%), 434.96 (1.3%), 435.95 (1.0%). Lipinski rule = 427.965; 4; 2; 1; 0.

2.4 | Molecular composition of the CT complexes

The method of continuous variation, a technique first developed by Job, was applied to determine the molecular composition (stoichiometry) of the formed CT complexes. The plot of absorbance versus mole fraction revealed that the maximum absorbance was recorded at 0.5 mole fraction, which indicates the formation of a 1:1 CTC_1 and CTC_2 complexes in acetonitrile and methanol solvents, respectively. These photometric titrations were measured for the reactions of the BZ donor with DDQ and CHL acceptors at 457 and 443 nm, respectively. A 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, and 4.00 ml aliquots of a standard solution (5.0×10^{-4}M) of the appropriate acceptor in solvent were added to 1.00 ml of BZ (5.0×10^{-4}M). The total volume of the mixture was set to 5 ml. The concentration of BZ (C_1) in the reaction mixture was kept fixed at 5.0×10^{-4}M while the concentration of the π-acceptors (C_2) changed over a wide range of concentrations from 0.25×10^{-4}M to 4.0×10^{-4}M, to produce solution varying ratio of donor to acceptor from 4:1 to 1:4. The stoichiometry of the molecular CT complexes was determined by the application of

conventional spectrophotometric molar ratio according to the known methods.

2.5 | Computational details

The Gaussian 09W[12] program was used for the density functional theory (DFT) calculations of the reactants and complexes in the gas phase. The geometries of the reactants (BZ, DDQ, and CHL) and CT complexes (CTC_1 and CTC_2) were fully optimized at Becke 3-parameter Lee-Yang-Parr hybrid exchange-correlation functional (B3LYP)[13] and 6-31 + G(d,p) basis set. We have used the GaussView 5.0.8 to draw the input molecular structures[14] and also to analyze the electron density distribution in frontier molecular orbitals.

3 | RESULTS AND DISCUSSION

3.1 | Electronic spectra

The absorption spectra of donor-acceptor mixtures were recorded, and the CT complexes were characterized by the appearance of new absorption band, which is attributed to the n-π* transition. Mixing of violet colored BZ with pale yellow–colored DDQ yielded a brownish mixture whose electronic absorption spectrum showed multiple CT bands at 423, 442, 457, 547, and 587 nm, which were not observed in the absorption spectrum of either donor or acceptor (Figure 1A). These transitions are attributed to the electronic transitions from more than 1 closely located HOMO to 1 or more LUMOs. The interaction of BZ with DDQ was allowed to continue at room temperature, and the absorption spectrum of the reaction mixture (CTC_1) was recorded against blank solution at 5-minute intervals. These bands are the characteristic absorption band of DDQ radical anion.[15] Further, the gradual decrease in intensity of these CT bands observed in the 400 to 600 nm spectral regions could be due to the consumption of the ion pair. Three peaks at 423, 442, and 457 nm disappeared and gave a stable peak at 441 nm, and there was not much difference between the peaks at 547 and 587 nm (Figure 1B).

The BZ solution was mixed with CHL solution, and the interaction of BZ with CHL was allowed to continue at room temperature, and the absorption spectrum of the reaction mixture was recorded against blank solution (Figure 2A). A violet-colored product was obtained that absorbs maximum at 443 nm, and absorption intensity of this new absorption maximum increased with time (Figure 2B). This gradual continuous increase in the new absorption band with the reaction time indicates the formation of the CT-complex CTC_2. The new absorption band was attributed to the complete electron transfer from the donor to acceptor accompanied by the formation of colored CHL radical anion,[16] which was formed

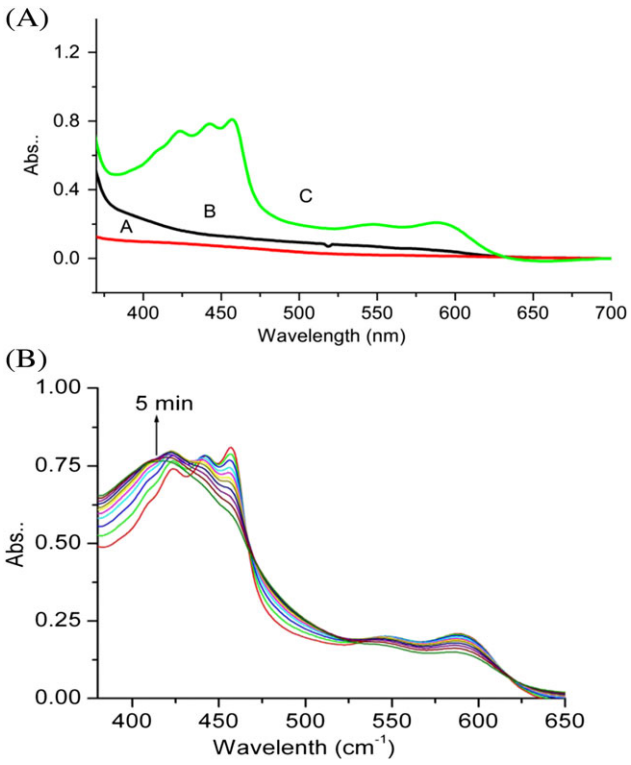


FIGURE 1 A, Electronic absorption spectra of the charge transfer complex (green), 2,3-dichloro-5,6-dicyano-p-benzoquinone (black), and benzidine (red) in acetonitrile. B, Absorption spectra of the reaction mixture (CTC_1) measured at varying time intervals (5-60 minutes) against the reagent blank in acetonitrile

by the dissociation of an original donor-acceptor complex. The observed absorbance of the CT complex was stable for more than 60 minutes at room temperature.

3.2 | Reaction with π-acceptors (DDQ and CHL)

The chemistry involved in the proposed method is based on the reaction of the donor (BZ) with the π-acceptors (DDQ and CHL) to form CT-complex, which subsequently dissociates to form radical anion depending on the polarity of the solvent used. The complete electron transfer from the donor to the acceptor moiety takes place with the formation of intense-color radical anion,[17] according to the following equation.

$$\underset{}{D:+A} \rightarrow \underset{\text{Charge transfer complex}}{[D:\rightarrow A]} \rightarrow \underset{\text{Radical anion}}{D^{\cdot+}+A^{\cdot-}} \quad (1)$$

The dissociation of the (D−A) complex is generally promoted by the high ionizing power of the polar solvent and the resulting peaks in the absorption spectra of the reaction mixture are similar to the maxima of the radical anion of the acceptor obtained from the reduction method.

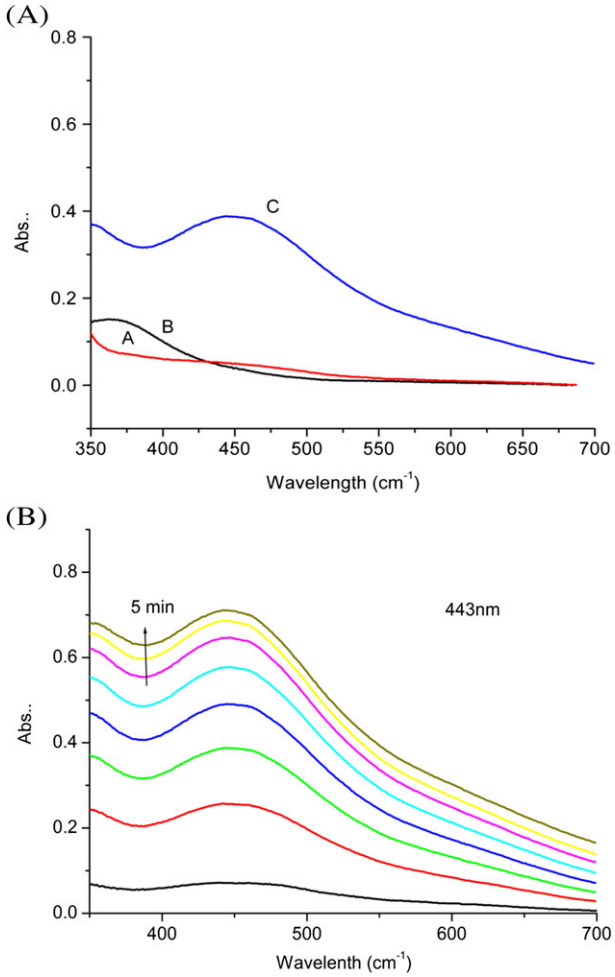


FIGURE 2 A, Electronic absorption spectra of the charge transfer complex (blue), chloronil (black), and benzidine (red) in methanol. B, Absorption spectra of the reaction mixture (CTC_2) measured at varying time intervals (5-60 minutes) against the reagent blank in methanol

3.3 | Composition of the CT complex

We have used the Job continuous variation method[18] to determine the composition (stoichiometry) of the formed CT complexes CTC_1 (DDQ and BZ) and CTC_2 (CHL and BZ). In this method, we have prepared several solutions in which the concentrations of the donor and the acceptor are varied but the sum of the concentrations is kept constant. Using these solutions, the absorption of the solutions is measured and plotted versus the mole fraction. The plots of CTC_1 and CTC_2 obtained from this method have been shown in Figures 3 and 4, respectively. From the figures, it can be observed that the maximum absorbance occurs at 0.50 mole fraction, which indicates 1:1 stoichiometry of donor to acceptor for CTC_1 and CTC_2. On the other hand, the 2 straight lines produced in the spectrophotometric titration[19] method are intercepting at 1:1 donor to acceptor ratio (Figures 5 and 6) that also confirms the 1:1 stoichiometry. The same

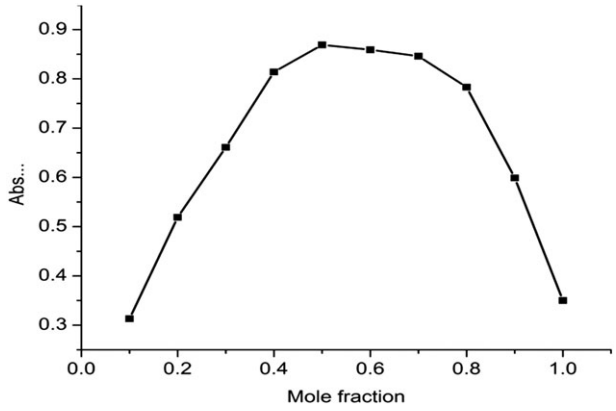


FIGURE 3 Job's plot of the charge transfer complex CTC_1

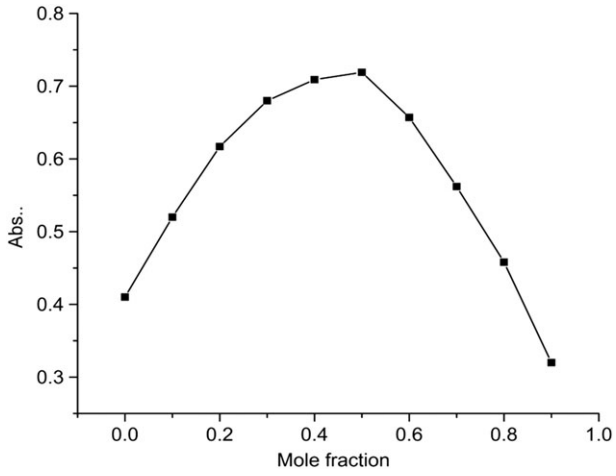


FIGURE 4 Job's plot of the charge transfer complex CTC_2. DDQ, 2,3-dichloro-5,6-dicyano-p-benzoquinone

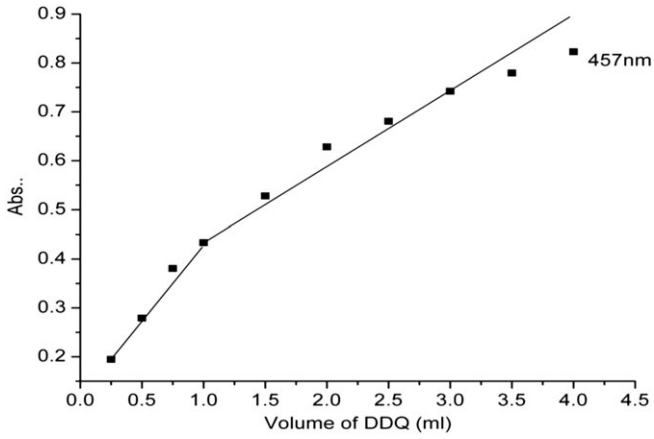


FIGURE 5 Photometric titration plot for CTC_1 system

stoichiometry of CTC_1 and CTC_2 systems was further confirmed by the modified Benesi-Hildebrand plots as shown in Figures 7 and 8.

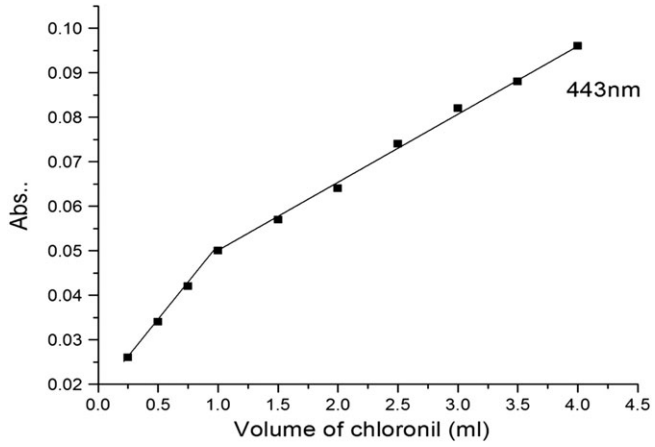


FIGURE 6 Photometric titration plot for CTC_2 system

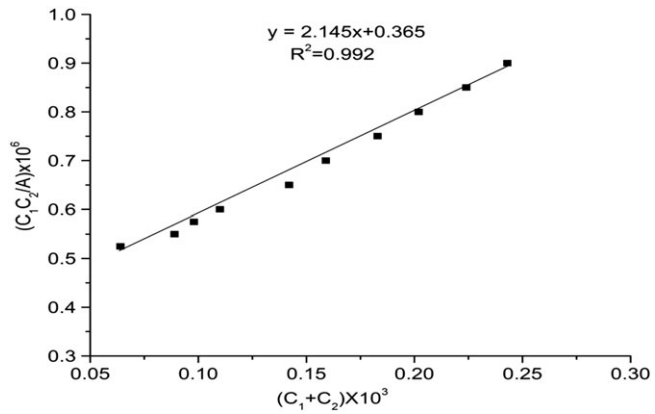


FIGURE 7 The modified Benesi-Hildebrand plot of CTC_1

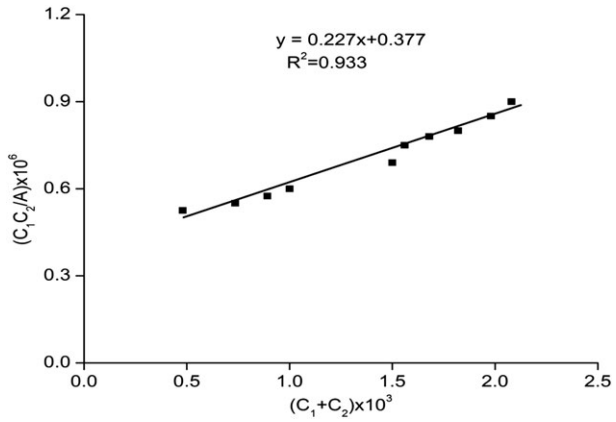


FIGURE 8 The modified Benesi-Hildebrand plot of CTC_2

3.4 | Formation constant and CT energy of CT complexes

The modified Benesi-Hildebrand[20] equation has been used to calculate the formation constant, K (L mol^{-1}) and molar extinction coefficient, ε (L mol^{-1} cm^{-1}) of the CT complexes.

$$\frac{\mathbf{C_1\ x\ C_2}}{\mathbf{A}} = \frac{1}{\mathbf{K_{CT}\varepsilon}} + \frac{\mathbf{C_1 + C_2}}{\boldsymbol{\varepsilon}}, \tag{2}$$

whereas C_1 and C_2 are the initial concentrations of π-acceptor (DDQ or CHL) and donor (BZ), respectively, A is the absorbance of the CT band. The data obtained for C_1 and C_2 then the values of $(C_1 + C_2)$ and $(C_1 \times C_2)/A$ were calculated. The plot of $(C_1 \times C_2)/A$ Vs $(C_1 + C_2)$ has been found to be a straight line with a slope of 1/ε and with an intercept of $1/K_{CT}\varepsilon$ (Figures 7 and 8). The K and ε values for CTC_1 and CTC_2 complexes were given in Table 1. The formation constant depends on the nature of the acceptor and donor.

3.5 | Determination of the spectroscopic physical data

The standard free energy of complexation (ΔG^0) for each complex has been calculated using the formation constant.[21] The free energy changes (ΔG^0) of CTC_1 and CTC_2 were calculated from the following equation and were given in Table 1.

$$\Delta \mathbf{G^0} = -\mathbf{RT\ lnK_{CT}} \tag{3}$$

The results of ΔG^0 reveal that the CT complex formation process is spontaneous. The ΔG^0 values are found to be more negative as the formation constant of the CT complex increases. As the bond between the components becomes stronger and thus the components are subjected to more physical strain or loss of freedom, the ΔG^0 value becomes more negative. The more negative value of ΔG^0, the farther to the reaction will proceed to achieve equilibrium.

The energy of charge transfer (E_{CT}) for CTC_1 and CTC_2 have been calculated by using the following equation:[21]

$$\mathbf{E_{CT}} = (\mathbf{h\upsilon_{CT}}) = \frac{1243.667}{\boldsymbol{\lambda_{CT}}}, \tag{4}$$

whereas λ_{CT} is the wavelength of the band (CT complexes). Generally, these complexes have a high formation constant and extinction coefficient. These high values of K confirm the expected high stabilities of the CT complexes because of the extensive donation from the BZ due to the amino groups. The formation constants also depend on the nature of the acceptors.

The IPs of the BZ donor in the complexes were calculated using the following empirical equation:[21]

$$\mathbf{IP\ (eV)} = 5.76 + 1.53\ \mathbf{x}\ 10^{-4}\ \upsilon_{CT}, \tag{5}$$

whereas υ_{CT} is the wavenumber in cm^{-1} that corresponds to the CT band formed from the interaction between the donor and the acceptor. The electron-donating power of the donor is measured in terms of its IP, the energy required to the

TABLE 1 Spectrophotometric and free energy change results of CT complexes

Complex	K_{CT} (L mol^{-1})	λ_{max} (nm)	$-\Delta G^{\circ}$ (kJ mol^{-1})	E_{CT} (eV)	ε (L mol^{-1} cm^{-1})	IP	W	R_N
CTC_1	5.872	457	−3671.43	2.72	0.446	9.12	4.5	0.777
CTC_2	4.424	443	−4355.99	2.81	0.602	9.21	5.03	0.802

removal of an electron from its HOMO. The dissociation energy (W) of formed CT complex was calculated from the corresponding CT energy (E_{CT}), the ionization potential of the donor (IP), and electron affinity (EA) of the acceptor.

$$\mathbf{W = IP - EA - E_{CT}} \tag{6}$$

Briegleb and Czekalla[22] theoretically derived the following relationship to obtain the resonance energy (R_N).

$$\varepsilon_{CT} = \frac{7.7 \times 10^{-4}}{h\upsilon_{CT}/[R_N] - 3.5}, \tag{7}$$

whereas ε_{CT} is the molar absorption coefficient of the CT complex at the maximum of the CT absorption, υ_{CT} is the frequency of the CT peak, and R_N is the resonance energy of the complex in the ground state, which contributes to the stability constant of the complex (a ground-state property).

3.6 | Infrared spectra

The IR absorption spectra of the BZ and the CT complexes CTC_1 and CTC_2 were recorded. The complete IR data are compiled in Table 2, and the spectra are shown in Figure 9. The donation process from the BZ to the π-acceptors can occur either from the lone pair of electrons on the nitrogen atom of amino groups or from the aromatic rings.[23,24] The nitrogen atoms have been identified as the donation source in most of the cases studied. The IR spectroscopy has been used to distinguish between the 2 possibilities. In this case, the υ(N–H), υ(C ≡ N), and δ(N–H) bands of BZ donor were shifted to lower frequencies on complex formation.

The IR spectrum of the molecular complex of DDQ with BZ indicates that the single υ(C ≡ N) of the free acceptor molecule that exhibited at 2250 cm^{-1} is shifted to a lower wavenumber of 2249 cm^{-1}, while the υ(C = O) absorption band of the free DDQ at 1674 cm^{-1} is shifted to lower value of 1653 cm^{-1} on complex formation.

Comparison of the IR spectral bands of the free BZ, frequencies at 3327 and 3194 cm^{-1} correspond to NH_2

TABLE 2 Characteristic infrared frequencies (cm^{-1}) and tentative assignments

BZ	DDQ	CTC_1	CHL	CTC_2	Assignments
3402 s		3196		3354	υ(H2O) KBr
		3401br		3424	m(O-H)
3327 ms				3219	υ (NH) BZ
3194					
3028				3019	υ_s(C–H)
2824		2851		2847	υ_{as}(C-H)
	2251	2249			υ(C ≡ N)DDQ
	1674	1653	1687	1686	ν(C = O), DDQ, chloronil
1607		1598		1590	δNH_2
	1583	1572	1588	1570	υ(C = C), DDQ, chloronil
1265		1273			υ(C-N)
1173					υ(C-C) BZ
820					υ(CH) out of plane waging
	750	743		752	NH deformation
700			711		υ(C-Cl) chloronil
509					υ(CH) out of plane bending BZ

Abbreviations: BZ, benzidine; CHL, chloronil; DDQ, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ); s, strong; m, medium; υ, stretching; υ_s, symmetrical stretching; υ_{as}, asymmetrical stretching; b_r, broad

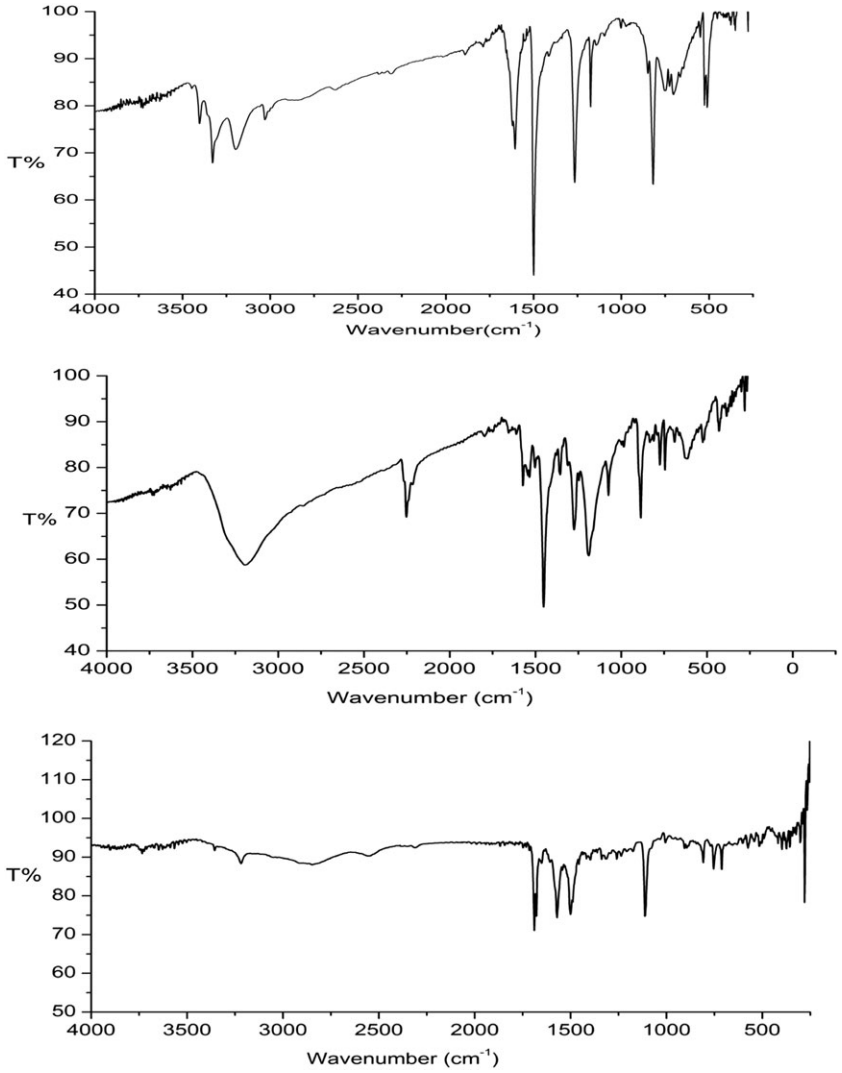


FIGURE 9 Fourier transform infrared spectra of the benzidine (top), CTC_1 (middle), and CTC_2 (bottom) in the range of 4000 to 400 cm^{-1}

asymmetric- and symmetric-stretching vibrations and these were found to be shifted and reduced in intensity after complexation. It shows that the -NH_2 group in the BZ participates in the complex formation process. It is known that the -CN group is an electron withdrawing group in DDQ in the conjugated system that pulls the electrons from the aromatic ring. It results in a decrease in bond strength of C N and subsequently lowers its vibrational wavenumber during the complex formation. Therefore, it can be concluded that the NH_2 group of BZ participates in complex formation with DDQ. Further, υ(C–Cl) of the free acceptor are also shifted to lower wavenumber values on complexation. From the IR spectrum of the molecular complex of CHL with BZ, it has been observed that the υ(C = O) of the free acceptor molecule that exhibited at 1686 cm^{-1} is shifted to a lower wavenumber value of 1685 cm^{-1}, while the υ(C = C) absorption band at 1588 cm^{-1} is shifted to a lower value at 1570 cm^{-1}. Since DDQ is derived from any acidic centers, thus we may conclude that the molecular complexes are formed through π–π* and/or n–π* charge migration from HOMO of the donor to the LUMO of the acceptor. The hydrogen bonding between the BZ proton (–NH_2) and the oxygen of the acceptor is strongly supported by the appearance of the characteristic peaks m(O–H) at the wavelengths of 3401 and 3424 cm^{-1} for CTC_1 and CTC_2 complexes, respectively.

3.7 | ^{1}H NMR spectra

The ^{1}H NMR spectra of the CT complex CTC_2 were recorded in DMSO and shown as Figure 10. Using the ^{1}H NMR studies, we have identified the nature of interactions between the donor and the acceptor of the resulted product shown in Scheme 1. The formation of the complex was confirmed by the appearance of new signals in the spectrum. The broad peak observed between 3.0 and 3.5 ppm in the spectrum of the CTC_2 is due to the formation of intermolecular hydrogen bond between the hydrogen of amine (-NH_2) of BZ and oxygen of the CHL. The peaks observed between 7 to 8 ppm are due to the aromatic nature of BZ.

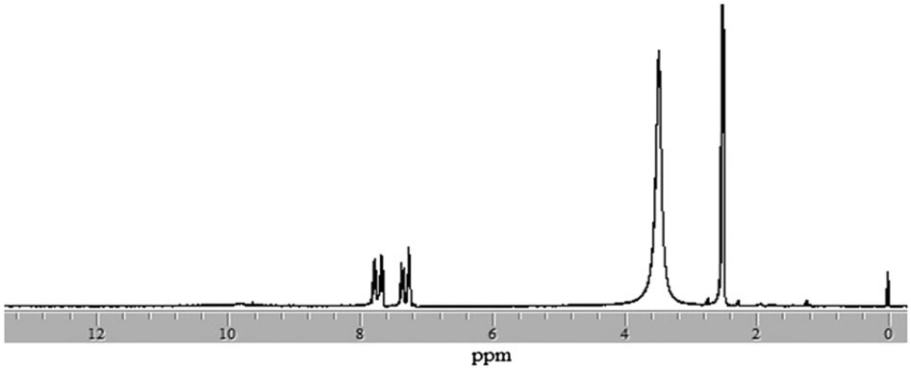
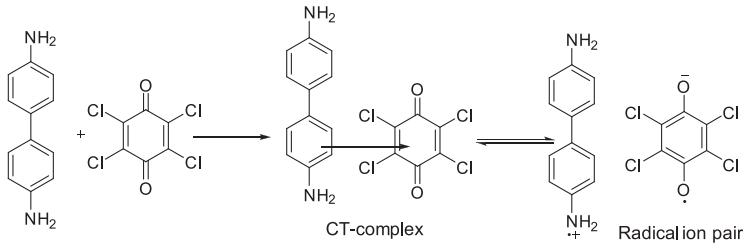


FIGURE 10 H^1 NMR spectra of the charge transfer complex CTC_2 obtained in dimethyl sulfoxide



SCHEME 1 Schematic representation of CTC_2 formation from benzidine and chloronil

4 | COMPUTATIONAL STUDIES

4.1 | Geometry optimizations and charge distributions

The molecular modeling studies have been conducted to confirm the formation of CT complexes (CTC_1 and CTC_2). The optimized bond lengths of BZ, DDQ, CHL, CTC_1, and CTC_2 complexes in the gas phase, calculated by DFT (B3LYP) method, are given in Tables **S1** and S2, and optimized geometries are shown in Figure 11. It has been observed that the C═O bond length in DDQ and CHL increased by 0.017 Å (from 1.240 to 1.257 Å) and 0.005 Å (from 1.238 to 1.243 Å), respectively. On the other hand, the C─Cl bond length in DDQ (1.780 Å) and in CHL (1.783 Å) has been increased upon complexation.[25] Interestingly, the C═C bond length in DDQ and in CHL is either increased or decreased upon complexation. The C─N bond length in DDQ increases upon complexation (from 1.173 to 1.174 Å). The most of the bond length parameters of BZ moiety are found to be decreased upon complexation.

The Mulliken atomic charges[26] play a vital role in the application of quantum mechanical calculations to the molecular systems, especially in CT phenomenon. In DDQ, the Mulliken charges on the C1/C2 and C4/C5 atoms were found to be 0.151 and −0.264 au while that of on carbon atoms attached to oxygen, ie, C3 and C6, was found to be 0.332 au. The Mulliken charges on the C1, C3, C4, and C6 atoms of CHL were found to be −0.260 au and while that of on carbon atoms attached to oxygen, ie C2 and C5, was found to be 0.393 au. The charges on Cl atoms of both CHL and DDQ were found to be decreased, and the charges on both the O atoms were found to be increased upon complexation. The charges on the C11, C12, N13, and N14 atoms in DDQ increased upon complexation. But on complexation with BZ, the charges were found to vary from atom to atom as depicted in Tables S3 and S4. The electronic charges of N21 and N24 in BZ were found to be −0.197 au, which were decreased upon complexation with DDQ to −0.079 and −0.101 au and also decreased upon complexation with CHL to −0.165 and −0.177 au. This indicates that appreciable amount of electronic charge has been transferred from BZ (donor) to DDQ and CHL (acceptors). Therefore, it can be concluded that the Mulliken charges increased for most of the atoms of the DDQ and CHL and decreased for most of the atoms of BZ upon complexation.

4.2 | HOMO-LUMO calculation for CTC_1 and CTC_2 complexes in the ground state

The HOMOs and LUMOs of the complexes CTC_1 and CTC_2 were obtained using the B3LYP method and are shown in Figures **S1** and S2. The electron density distribution pattern at BZ and DDQ/CHL can be observed from HOMO and LUMO. In CTC_1, HOMO, HOMO-2, and HOMO-3 were localized only on BZ. While for CTC_2, the electron density is localized only on BZ for HOMO, HOMO-2, HOMO-3, and HOMO-5 whereas it is localized on the CHL for HOMO-4.

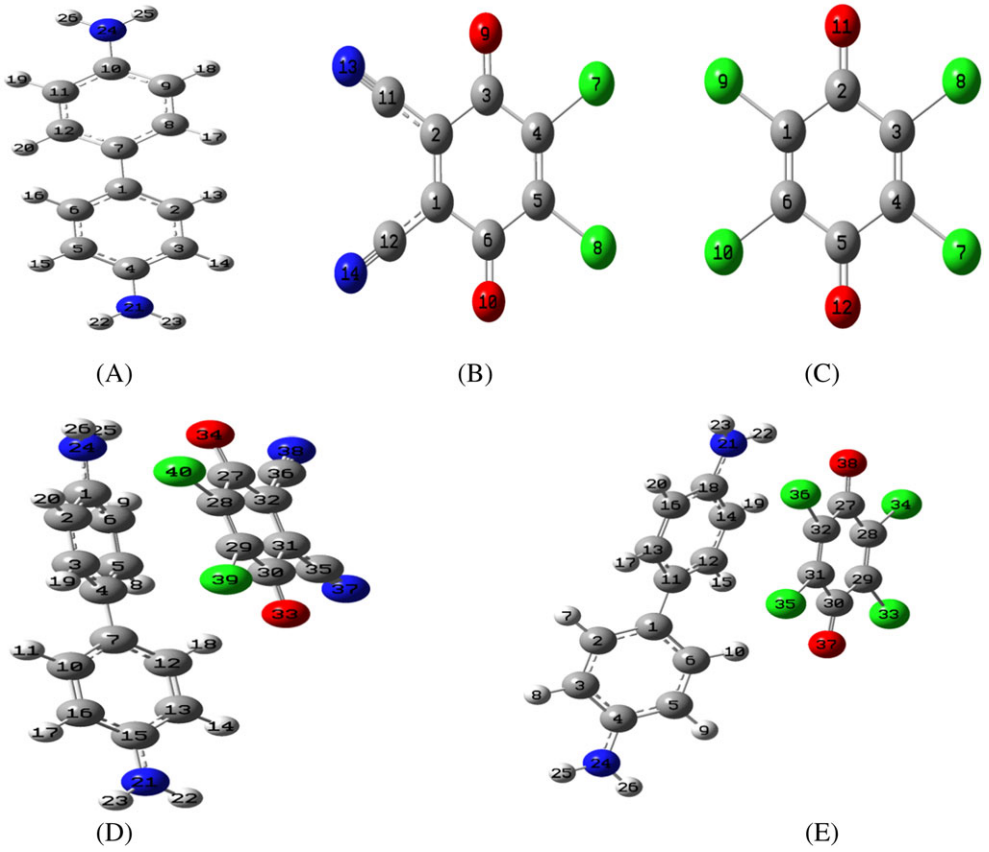


FIGURE 11 The optimized ground state geometric structures of (A) benzidine, (B) DDQ, (C) CHL, (D) CTC_1, and (E) CTC_2 obtained at B3LYP/6-31 + G(d,p) level

From Tables S5, it is interesting to note that the LUMO energy level of the CTC_1 complex (−0.17 eV) is in comparable with that of DDQ (−0.18 eV), whereas the HOMO energy level of the CTC_1 complex (−0.19 eV) is close to that of BZ (−0.18 eV). Similarly, from Tables S6, it has been observed that the LUMO energy level of the CTC_2 complex (−0.16 eV) is in comparable with that of CHL (−0.18 eV), whereas the HOMO energy level (−0.18 eV) of the CTC_2 complex is close to that of BZ (−0.18 eV). This tendency for localization of frontier molecular orbitals of CTC_1 and CTC_2 systems is very much similar to the previously reported electron donor-acceptor composite systems.[27,28] From the above discussion, it is very clear that the orbital interaction energy arises mainly from the CT between occupied and unoccupied orbitals. The molecular electrostatic potentials (MEPs) are useful for correlation of the relative orientation of the acceptor and donor molecules in the formation of CT complex.

4.3 | Molecular electrostatic potential

The MEP[29] is the most convenient electrostatic property to study the relation between structure and activity of a molecule that describes the interaction energy between the electrical charges generated from electron and nuclei of the molecule.[30] The MEP maps are used to visualize variably charged regions of a molecule[31] and is a good guide to assess the reactivity of the molecule towards positively or negatively charged reactants. The different values of the electrostatic potential are represented with different colors. The red, blue, and green colors represent regions of most electronegative, most positive, and 0 electrostatic potentials, respectively. The electrostatic potential increases in the order of, red < orange < yellow < green < blue.

Significant changes have been observed for the complex moieties (CTC_1 and CTC_2) compared to either BZ or DDQ or CHL, confirming the CT route. The MEPs were computed at the same level of theory as used for the geometry optimization. As shown in Figure 12, the MEP plot of DDQ was characterized by a positive region (blue) that is localized on the center of the 6-membered ring with a surface map value of 0.06305 au while the regions of negative potential were observed around the nitrogen atoms (−0.03671 au) of the cyano groups and oxygen atom of the carbonyl group (−0.02628 au). For the BZ, the negative potential (−0.03691 au) is mainly associated with the center of the benzene rings due to the presence of π-electrons and donation of lone pair electrons of the amine group, a positive potential (0.04376 au) was located on the N atom of the amine groups (Figure 12A). In CTC_1, where the BZ interacts with DDQ,

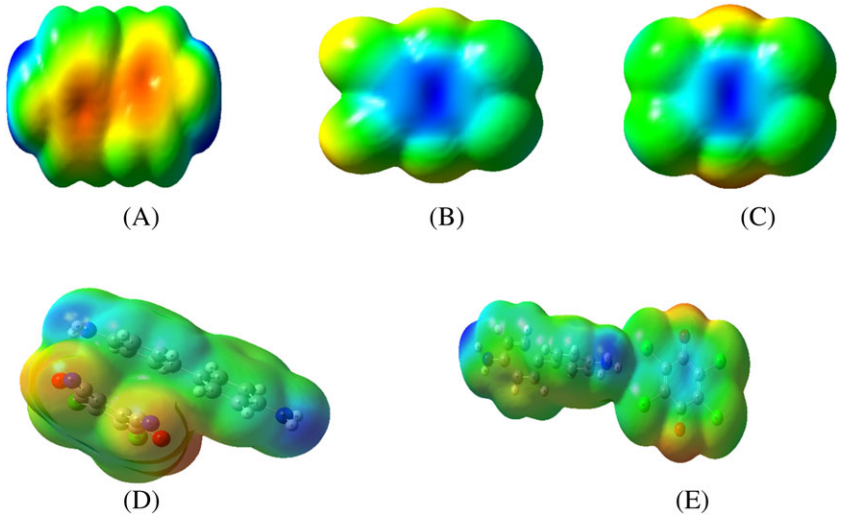


FIGURE 12 Molecular electrostatic potential maps for (A) benzidine, (B) 2,3-dichloro-5,6-dicyano-p-benzoquinone, (C) chloronil, (D) CTC_1, and (E) CTC_2 in ground state obtained from density functional theory calculations

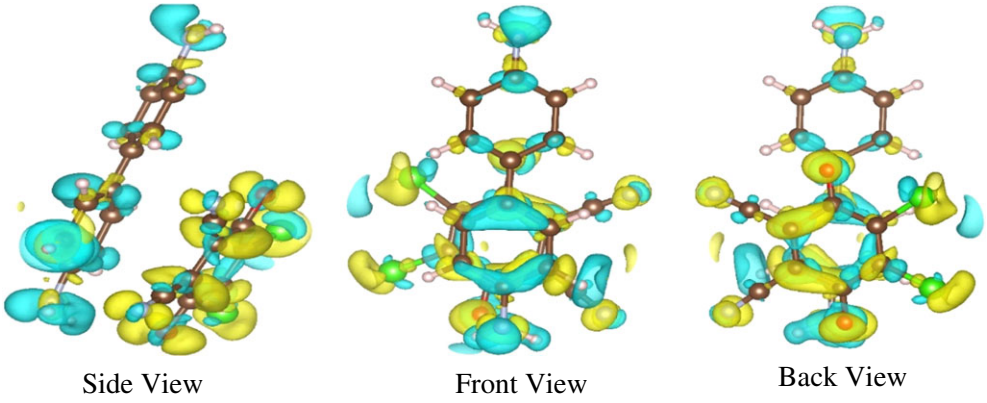


FIGURE 13 The charge density difference plot of the charge transfer complex CTC_1

the center positive value of DDQ decreased to 0.02130 au, N atom of cyano group potential and O atom of the carbonyl group potential increased to −0.05063 and −0.04245 au, respectively. The center of the benzene ring potential decreased to −0.00800 au and N atom of amine group in BZ potential increased to 0.04909 au upon the CT interaction (Figure 12D). In CHL, a positive region (blue) was localized on the center of the 6-membered ring with a maximum surface value of 0.04754 au while the region of negative potential (red) was observed around the oxygen atom of the carbonyl group (−0.03466 au). In CTC_2, where the BZ interacts with CHL, the center surface value of CHL decreased to 0.03310 au. The O atom of carbonyl group potential (−0.04106 au) and N atom of amine group in BZ potential (0.04958 au) increased upon the CT interaction (Figure 12 E). These results further reinforce the concept that DDQ and CHL are generally considered as good electron acceptors in forming CT complexes with various donors.[32]

The charge density difference plot of the CT complex CTC_1 has been given in Figure 13. The yellow region represents charge accumulation whereas the light blue region represents the charge depletion. From the figure, it has been clearly observed that the charge is deposited on DDQ and is depleted from BZ molecule upon the formation of CT complex.

5 | CONCLUSIONS

Charge transfer reactions of BZ with the DDQ and CHL were investigated experimentally and theoretically. The spectroscopic and physical parameters of these complexes were evaluated. Ultraviolet–visible, IR, and ^{1}H NMR spectra were used to characterize the complexes in solution and solid states. The computational investigation has been conducted using DFT calculations. The computed geometrical parameters (bond lengths) have shown variation for the complexes as compared with those of individual reactants. The Mulliken atomic-charge analysis revealed that the increased values for the acceptor and the decreased values for the donor in the complex as compared with the corresponding isolated species, asserting the CT-complex formation. In addition, the suggested positioning of the acceptor molecule with respect to the donor molecule was confirmed theoretically from the

HOMO, LUMO, and MEP calculations. The orientation of the donor (BZ) to the acceptors (DDQ and CHL) in CT complexes is mirrored in MEPs. The obtained experimental results were in good accordance with the computational study. From the results, it is concluded that the CT is taking place from BZ to DDQ and BZ to CHL.

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