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Original Article

Molecular Charge-Transfer Complex between Thymol Drug and Bromocresol purple

Asmaa Abd Aziz Ibrahim[1], El-Sayed Hossani El-Mossalamy[2], Safaa Abdel-Aal[3]

[1]Assistant Professor, Department of Chemistry, Aswan University, Aswan, Egypt
[2]Professor & [3]Assistant Professor, Department of Chemistry, Banha University, Banha, Egypt

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ABSTRACT

The charge-transfer complex of the thymol (TY) {2-isopropyl-5-methylphenol} Drug with {4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3-ylidene)- bis(2-bromo-6-methylphenol)} Bromocresol purple (BCP) were studied spectrophotometrically in different solvents. Using application Benesi-Hildebrands equation, molar extinction coefficient (εCT), the equilibrium constant (KCT) and thermodynamic parameters were estimated. The geometric parameters, electronic properties and molecular electrostatic potential were calculated. Elemental analyses (CHN) IR, UV–Vis techniques investigation were used to characterize and conforms the molecular structure of thymol CT-complex. Quantum chemical calculations have been carried out by using density functional theory and time-dependent density functional theory calculations.

Keywords: Thymol, spectrophotometry, formation constant, molar extinction coefficient, quantum chemical calculations.

INTRODUCTION

CT-complexes of organic are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor [1,2] Also, protonation of the donor from acidic acceptors are generally rout for the formation of ion pair adducts [3-5]. CT-complexes are occur between acceptors, having sufficiently high electron affinity and electron donors, having sufficiently low ionization potential. The transfer of an electron from a donor to an acceptor is readily possible in the charge transfer process (6). Charge transfer complexes formed between Pantoprazole (donor) and chloranilic acid (CHLC), (DDQ) (acceptors) [7]. Charge transfer complexes of donor as Schiff bases with acceptors as picric acid and m-dinitrobenzene were investigated by using computational analysis calculated by Configuration Interaction Singles Hartree-Fock (CIS-HF) at standard 6-31G basis set and Time-Dependent Density-Functional Theory (TD-DFT) levels of theory at standard 6-31G basis set, , visible, infrared and nuclear magnetic resonance spectra are investigated [8]. CT complexes formed between sulfadiazine as a donor and nitro compounds as a π-acceptors are studied [9].

Thymol (TY) {2-isopropyl-5-methylphenol}; is a natural monoterpene phenol derivative of cymene, is part of a naturally occurring class of compounds known as biocides, with strong antimicrobial attributes when used alone or with other biocides such as carvacrol. Additionally, naturally-occurring biocidal agents such as thymol can reduce bacterial resistance as penicillin. The antimicrobial effects of thymol, ranging from inducing antibiotic susceptibility in drug resistant pathogens to powerful antioxidant properties [10]. Charge-transfer complexes between the thymol as a donor and picric acid, chloranilic acid,1,3-dinitrobenzene or *p*-chloranil as a π-acceptor have been structurally and thermally studied in methanol at room temperature [11]. Determination of isoniazid, mesalazine, salbutamol and thymol drugs based on the charge-transfer (CT) complex formation reaction with o-chloranil as π-acceptor by spectrophotometric method [12].

Bromocresol Purple (BCP) {4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3-ylidene)-bis(2-bromo-6-methylphenol)}, is a pH indicator. It has a pKa value of 6.3 and is usually prepared as a 0.04% aqueous solution. Bromocresol purple is used to measure albumin and in photographic processing as an indicator that the bath has reached neutral pH and needs to be replaced [13]. The formation of complexes between escitalopram and

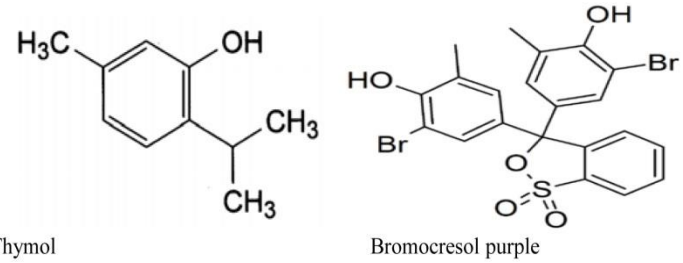
***Corresponding Author Address:** Dr. **Asmaa A. Ibrahim,** Assistant Professor, Department of Chemistry, Aswan University, Aswan, Egypt*
e-mail: doc_somaia@hotmail.com

sulphonphthalein acid dyes, namely; bromocresol purple, bromophenol blue, bromocresol blue, and bromocresol green in chloroform [14]. Herein, the CT interaction between the bromocresol purple with thymol (drug) was investigated. The nature and structure of the products have been characterized to interpret the behavior of interactions using infrared, electronic spectra and elemental analysis. The spectroscopic data were analyzed in terms of molar extinction coefficient (εCT) and formation constant (KCT). The thermodynamic parameters (ΔG°), (ΔS°) and (ΔH°) of CT complex formation from donor and acceptor were also calculated. Computational calculations were carried out for the complex.
Thymol Bromocresol purple

Aims and Objectives: Preparation of charge transfer complexes from thymol. Determination of hysical parameters of charge transfer complexes.

MATERIALS AND METHODS

Chemistry: All chemical used were of high grade. The thymol ($C_{10}H_{14}O_2$, Mol.Wt.= 150.22, M.p.= 51 °C,white crystalline) and bromocresol purple ($C_{21}H_{16}Br_2O_5S$, Mol.Wt.= 540.22, M.p.= 240° C, purple crystalline powder) were obtained from Sigma-Aldrich Chemical Company. Methanol, acetone, benzene and chloroform were obtained from Merck analytical grade and were used without further. The structures of donor and acceptor were presented in Formula I.



Thymol Bromocresol purple

Formula I. Structure of thymol (TY) and bromocresol purple (BCP).

The electronic absorption spectra were recorded in the region of 250–700 nm using UV–vis.spectrophotometer model JASCO V-530 with quartz cell of 1.0 cm path length. The infrared spectra of the reactants and the obtained complexes were recorded using KBr discs on either Perkin-Elmer 1430 or Buck Scientific 500 Infrared Spectrophotometer Elemental analyses were carried out in microanalysis unit of Cairo University, Egypt.

Methods

Reaction Procedure: The solid CT complex was prepared by mixing the solution of thymol (TY) (0.4507 gm,3mmol) in 20 ml methanol with saturated solution of bromocresol purple (BCP) (1.6207gm,3mmol) in 20ml methanol. Mixtures were stirred for around 12 hours and allowed to evaporate slowly, which resulted in the precipitation of the solid charge transfer complex. The separated CT-complex were filtered off, washed with little amounts of solvent and then collected and dried under vacuum over anhydrous calcium chloride.

Photometric titration: Photometric titration measurements were carried out for the reactions of TY with BCP in different solvents. X= 0.25, 0.50, 0.75, 1.00, 1.50, 2.0, 2.50, 3.00, 3.50 or 4.00 ml aliquot of a standard solution ($5.0x10^{-4}$ M) of the BCP was added to 1.00 ml ($5.0x10^{-4}$ M) of TY drug, TY and BCP were dissolved in benzene, chloroform and acetone. The total volume of the mixture was 5 ml to produce solutions with molar ratio varied from 4:1 to 1:4. The concentration of the TY ($5.0x10^{-4}$ M) and BCP (0.25x10-4 M to $4.00x10^{-4}$ M). In use of methanol, the concentration of the TY ($5.0x10^{-5}$ M) and BCP ($0.5x10^{-5}$ M to $5.00x10^{-5}$ M). X=2.00, 2.50, 3.00, 3.50, 4.00, 4.50 or 5.00 ml of BCP was added to 2ml of TY. The stoichiometry of the molecular CT complexes was obtained from the determination of the conventional spectrophotometric molar ratio according to known methods [15] using a plot of the absorbance of charge transfer complex as a function of the *Cd*:*Ca* ratio. Modified Benesi–Hildebrand plots [16] were constructed to allow the calculation of the formation constant, KCT, and the absorptivity, εCT, values for each CT complex.

Computational Method: Calculations were performed at B3LYP/SDD basis sets using the Gaussian 09W program [17]. The molecular behavior study by MEPs, the PDOS as well as Fermi levels were calculated by using the Gauss Sum 2.2.5 program [18] at the B3LYP/SDD level of theory.

Elemental analyses: Elemental analyses (C, H, and N) of the TY charge transfer complex were performed, and the obtained analytical data are as follows:

TY/BCP: C21H16N3Br2O5S, Mol.Wt.= 690.44, M.p.= 270^{O}C, color: light brown.

Anal. Calcd.: %C, 36.531; %H, 2.336; %N, 6.086.

Found: %C, 36.501; %H, 2.570; %N, 6.331.

Observation and Results

IR spectra: The infrared spectra of the TY solid charge transfer complexes were recorded in the frequency range 4000-400 cm-1 using KBr disc. The spectra of the TY/BCP complex are shown in Figure 1, the bands of TY and BCP observed at 3613 and 3481cm^{-1}, which is assigned to ν(O-H) stretching vibration, shifted to 3487 cm^{-1}and reduced in intensity after complexation. Also, the IR spectra of the complex are characterized by weak bands that appear at 2952 cm^{-1}, which does not appear in the spectra of the free TY donor or BCP acceptor. These peaks are due to hydrogen bonding in the complex formed through the transfer of a proton from BCP to -OH group of the TY donor [19]. These observations clearly indicate that the complexation occurs through the transfer of proton from the BCP to the TY donor, lone pair of electrons on the O to form +OH based on acid–base theory [20,21]. The bands in free BCP were shifted to lower wavenumbers (ν(C-Br) vibration to 767 and 726 cm^{-1}, ν(C-S) vibration to1189 cm^{-1} and also decreasing in the intensities of the characteristic peaks.

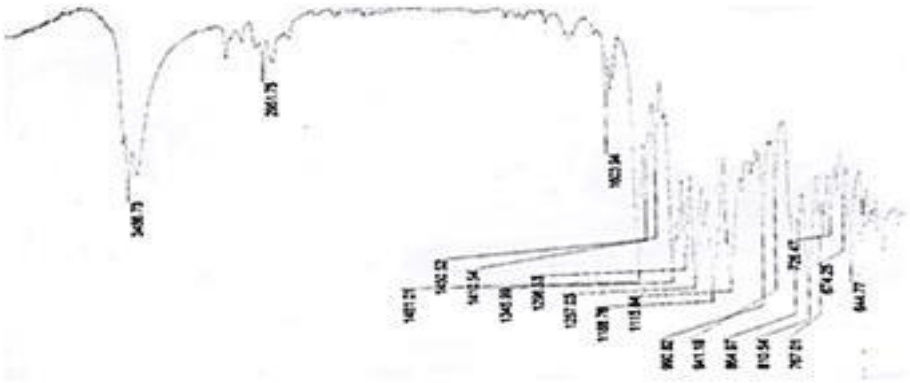
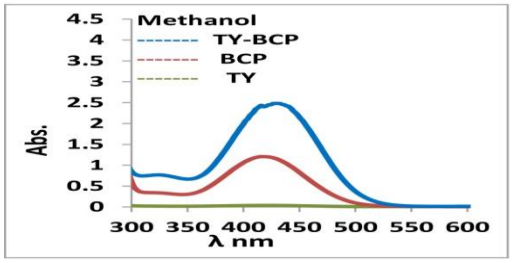
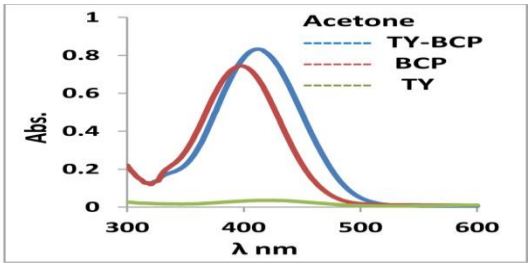


Figure 1. Infrared spectra of TY/BCP complex.

Electronic absorption spectra: Reactions of TY with BCP in polar and non-polar solvents, resulted in the formation of stable charge-transfer complex with a donor–acceptor ratio of 1:1. Electronic absorption spectra were obtained from 1x10^{-4} M solutions of complex TY/BCP in benzene (1), chloroform (2), and acetone (3) respectively, 2x10^{-5} M solutions of complex in methanol (4). The band maximum of TY under 300 nm and BCP at 408 nm (1), 404 nm (2), 398 nm (3) and 420 nm (4). In comparison with reactants spectra, new absorption bands at about 399 nm (1), 412 nm (2), 416 nm (3) and 430 nm (4) revealed CT-complex formation (Figure 2 and Table-1). Chloroform was found to be the suitable solvent for CT complex formation.

Composition of the CT-complex: The photometric titration measurements based on the absorption bands of the charge transfer complex (Figure 3) confirmed the complex formation in a ratio of 1:1. Examination and comparison of the absorption spectra of the TY, BCP, TY/BCP system shown that the spectra of TY/BCP are characterized by a maximum absorption at the CT-interaction. These peak absorbance values that appeared in the spectra assigned to the formed CT complex were measured and plotted as function of the *Cd*:*Ca* ratio according to the known method. Photometric titration plots based on these measurements confirmed the complex formation at a ratio (TY:BCP) of 1:1.





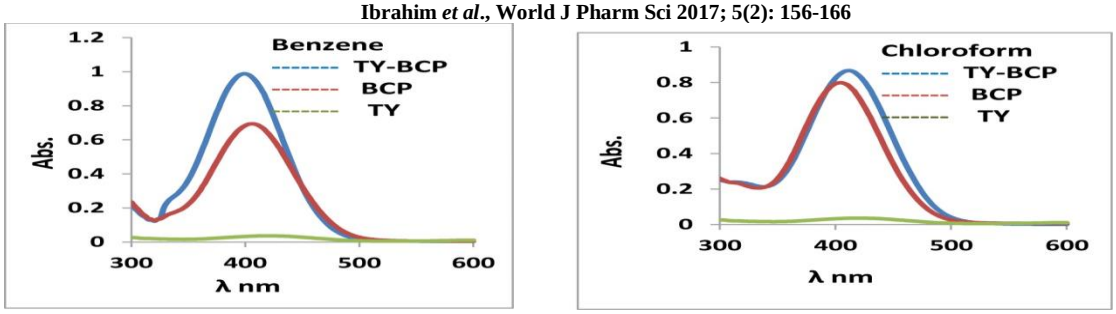


Figure 2. Electronic absorption spectra of TY/BCP CT complex in different solvents

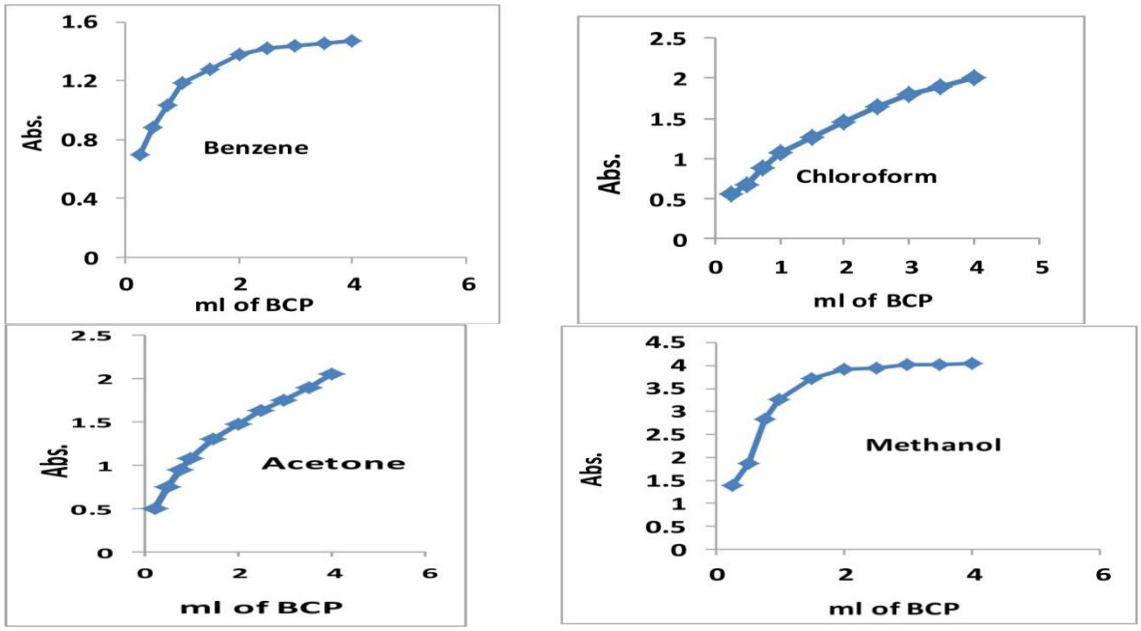


Fig. 4. The modified Benesi-Hildebrand plot of TY/BCP complex in solvents.

Determination of Formation constants of the CT complex: The formation constant (*KCT*) and the molar absorptivity (*εCT*) of the complexes were calculated by applying the 1:1 modified Benesi–Hildebrand equation [16]:

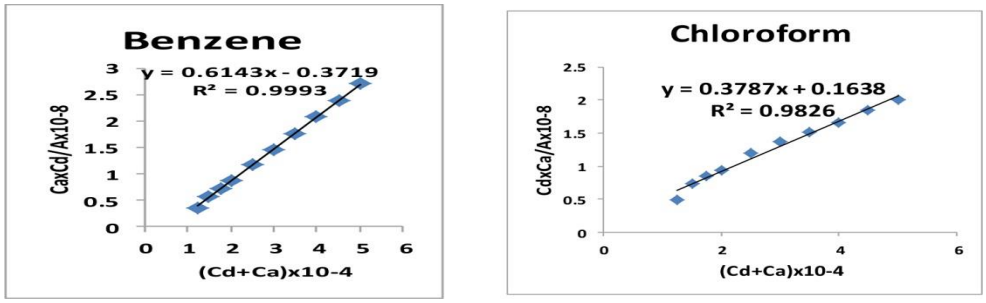
CaCd/A = 1/ε (Ca + Cd) + 1/Kε

where *Ca* and *Cd* are the initial concentrations of the acceptor and the donor, respectively and *A* is the absorbance of the CT band.

Plot of (CaCd)/A Vs (*Ca+Cd*) gave straight line with slope = 1/ εCT and intercept = 1/K εCT

KCT = intercept/ slope = 1/K εCT /1/ εCT

The modified Benesi–Hildebrand plots are shown in Figure 4 and the values of both K_{CT} and ε_{CT} associated with the complex in different solvents are given in Table-1. The CT-complexes exhibit high values of both the formation constant (K_{CT}) and the extinction coefficients (ε_{CT}). These high values of K_{CT} reflect the high stabilities of the formed charge transfer complexes. The equilibrium constants are strongly dependent on the nature of the used acceptor including the type of electron withdrawing substituents to it such as halo group [22] and high donation power of TY from two donating groups, the hydroxyl and three methyl groups [11].



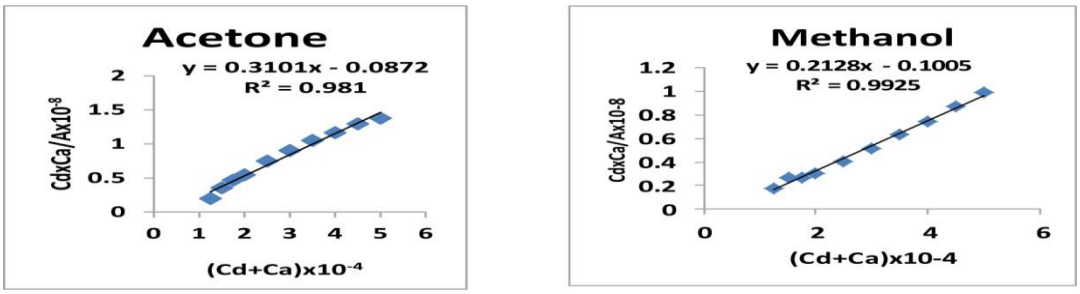


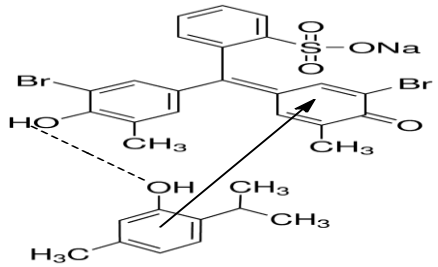
Fig. 4. The modified Benesi-Hildebrand plot of TY/BCP complex in solvents.

Table 1. Effect of solvents on the position and intensity of absorption of the complex.

Solvent	Dielectric constant	λ_{CT} nm	$K_{CT}x10^3$ Lmol $^{-1}$ cm	ε_{CT} $x10^3$ Lmol $^{-1}$ cm
Chloroform	**4.89**	**412**	**18.930**	**26.406**
Benzene	**2.27**	**399**	**16.549**	**16.278**
Acetone	**20.7**	**416**	**20.667**	**32.247**
Methanol	**32.7**	**430**	**21.200**	**46.992**

Discussion

The results indicate that the formation of charge transfer complexes between TY with BCP in methanol as a solvent, the elemental analysis data for the CT-complex are in agreement with the molar ratio obtained from the spectrophotometric titrations. The stoichiometry of TY donor with the BCP acceptor was found to have a 1:1 ratio. From IR data, the charge complex transfer can be concluded to form through n-π* charge migration from the HOMO of TY to the LUMO of BCP. The π-π* CT- complex is formed via the benzene ring (electron-rich group) of the donor and the acceptor (Formula II)



Formula II. Molecular structure of charge transfer complex of TY and BCP

Thermodynamic Parameters: The thermodynamic parameters (ΔG°, ΔS° and ΔH°) associated with the charge transfer complex formation of donor with acceptor in chloroform were determined and collected in Table-2 and Figure 5. The ΔH^o and ΔS^o values calculated using the equation derived by Van't Hoff equation:

ln KCT = - ΔH°/RT + ΔS°/R

A plot of ln KCT vs. 1/T gave a straight line from the slope and from intercept of which ΔH^o and ΔS^o were determined.

The Gibbs free energy Δ*G*^{o} at 20^o C were calculated from:

ΔG° = -RT ln KCT

Where Δ*G*° is the free energy change of the CT complex (Jmol^{-1}), the enthalpy ΔH° and entropy changes of complexes Δ*S*°, R is the gas constant (8.314 Jmol^{-1}K), T is the absolute temperature in K, and KCT is the formation constant of the complex (Lmol^{-1}). The negative values of the free energy (ΔG°) and the positive entropy change (ΔS°) suggesting the spontaneous production of the complexes formation. Negative values of (ΔH°) indicated that the reaction is exothermic. Further evidence for the nature of CT interactions is the calculation of the standard free energy (Table-2).

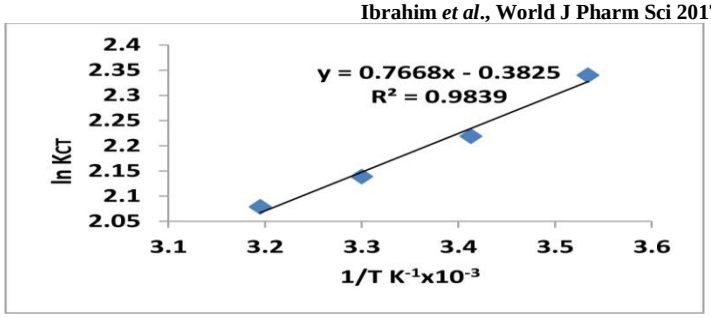


Fig. 5. Van t'Hoff plot for TY/BCP complex in chloroform for the CT complex in chloroform.

Table 2. Thermodynamic parameters and equilibrium constants

T (K)	1/T x10 $^{-3}$ (K^{-1})	K_{CT} x10^3 $Lmol^{-1}$ cm	ln K_{CT}	-ΔH° (KJ/mol)	ΔS° (J/mol.K)	-ΔG° (KJ/mol)
283	**3.534**	**20.399**	**9.923**	**14.302**	**32.455**	**23.992**
293	**3.413**	**18.930**	**9.849**			
303	**3.300**	**15.058**	**9.620**			
313	**3.195**	**11.448**	**9.346**			

Quantum chemical calculations: The quantum chemical calculations have been performed at B3LYP/SDD basis sets using the Gaussian 09W program by Frisch et. al [17]. The optimized molecular structures of TY, BCP and TY/BCP complex are shown in Fig. 4. The calculated geometric parameters can be used as foundation to calculate the other parameters for the compounds. The theoretical results obtained are almost comparable with the reported structural parameters of the similar molecule study by Montis et al [23]. The experimental and theoretical data shows that the C–C bond lengths are observed in the range 1.369–1.412 Å. The other values show that our calculated results are consistent with the experimental data. The analysis of frontier molecular orbitals describes one electron excitation from the highest occupied molecular orbital. The optimized geometry of the donor (TY) along with HOMO and the acceptor (BCP) along with LUMO are depicted in Figure 6. Cho and Tejerina et al [24,25] the energies of the frontier orbitals of the donor and the acceptor along with the energy corresponds to the CT transition, ΔE=HOMO donor–LUMO acceptor) are represented in Table-3.

Table 3: The HOMO, LUMO, energy gap (Eg), formation energy (ε/eV), ionization potential (IP/eV), electron affinity (EA/eV), chemical hardness (η/eV), and electronegativity (χ/eV), and electrophilicity (ω/eV) of the TY, BCP and TY/BCP complex.

compound	HOMO	LUMO	Eg	ε	IP	EA	η	χ	ω	S
TY	-5.994	-0.149	5.845		5.994	0.149	2.922	3.072	1.615	0.171
BCP	-6.605	-2.522	4.083		6.605	2.522	2.042	4.563	5.100	0.245
CT	-5.506	-2.834	2.672	-0.652	5.506	2.834	1.336	4.170	6.509	0.374

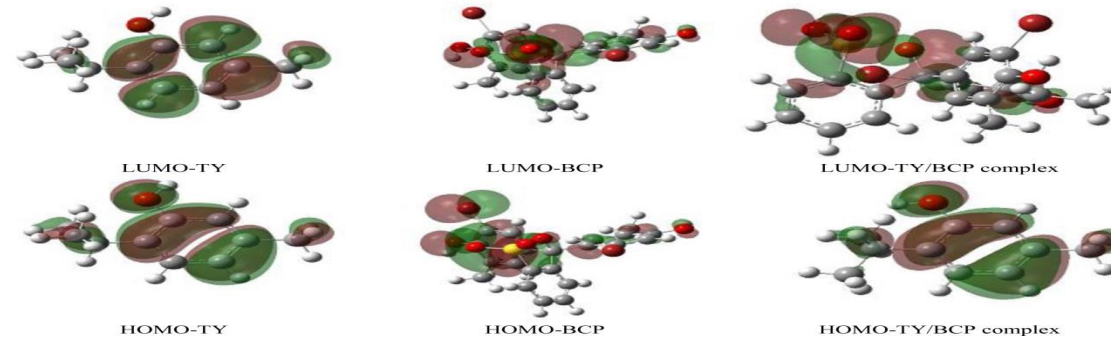


Figure 6: The optimized structures of TY, BCP and TY/BCP complex with frontier orbitals.

Electronic properties: The electronic descriptors, formation energy (ε), ionization potential (IP), electron affinity (EA), chemical softness (S), electronegativity (χ), chemical hardness(η) and electrophilicity index (ω) of the TY, BCP and TY/BCP complex were considered in Table 4. Parr and Yang [26] can be calculated the IP and EA from the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital energies using Koopmans approximation, where

$$IP = HOMO \text{ and } EA = LUMO$$

Parr and Yang [26] are derived the chemical potential (μ) and (χ) as

$$\mu = -\chi = -2IP + EA/2$$

Pearson [27] introduced two parameters, chemical hardness (η) and chemical softness (S) to account for the stability of a molecule. Chemical hardness (η) can also be expressed in terms of HOMO and LUMO and implying a finite difference approach [26] as follows:

$$\eta \approx IP + EA/2 \approx E_{LUMO} - E_{HOMO}/2$$

Yang et al [28] calculated the softness (S) as

$$S = 1/2\eta$$

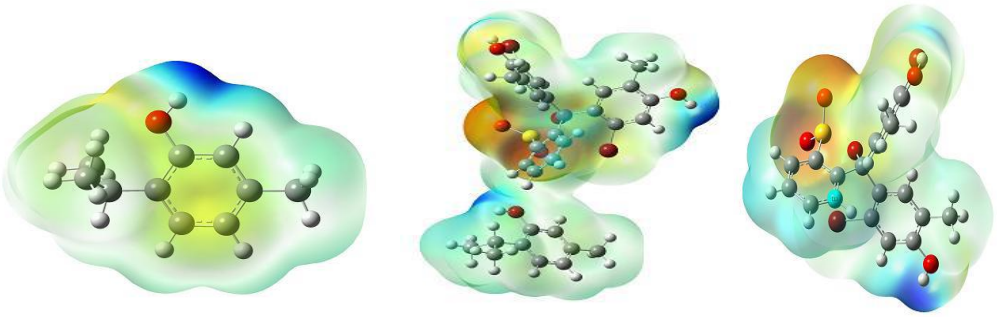
Parr [29] defined electrophilicity index (ω) as:

$$\mu^2/2\eta = \chi^2/2\eta$$

Which measures the energy stabilization when the molecule accepts an additional electrical charge from the environment. It is noted that a lower energy gap (E_g) between the LUMO and HOMO of a compound implies a greater and easier possibility of the electron transition between these energy levels. Additionally, a small value for E_g for the compound is an indicator of lower chemical stability. In other words, the respective chemical hardness should be low and electrophilicity (ω), which is a parameter indicating reactivity, should be high. The results presented in Table-4 show that the TY/BCP complex shows a notably lower value of E_g and η and a maximum value of electrophilicity compared to the TY and BCP. The electrophilicity index (ω) is one of the DFT based parameters which quantifies how reactive a molecule or compound. It is clear from the present analysis that the lower E_g and η values and higher value for the TY/BCP complex implies its favorable nature for the possible electronic transport and conductivity.

Molecular electrostatic potential: Wang et al [30] assumed that the molecular electrostatic potentials MEPs have been established extensively as a guide to the interpretation and prediction of molecular behavior. Naray and Murray et al [31] study both electrophilic and nucleophilic processes, in particular the "recognition" of one molecule by another Molecular electrostatic potentials are either negative, low potentials that are characterized by an abundance of electrons and reactive with electrophiles, or positive, high potentials that are characterized by an absence of electrons and reactive with nucleophiles. It is common to denote the former by red color, and the later with blue color. The different values of the electrostatic potential

at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The color code of these maps in compounds, where blue indicates the strongest attraction and red indicates the strongest repulsion. As can be seen from the MEP map of the title molecules, while regions having the negative potential are over the electronegative atom (in oxygen atom), the regions having the positive potential are over the hydrogen atoms. A maximum positive region localized on the H atom. From these results, we can say that the H atoms indicate the strongest attraction and O atom indicates the strongest repulsion. Figure 7 provides a visual representation of the chemically active sites and comparative reactivity of the atoms.



TY BCP TY/BCP complex

Figure 7: The MESP map of TY, BCP and TY/BCP complex.

The projected density of states (PDOS): The projected density of states (PDOS) of CT complexes describes the number of states per interval of energy at each energy level which are available to be occupied by electrons. A high PDOS at a specific energy level means that there are many states available for occupation, and therefore scales linearly with the interaction of CT complexes. In Figure 8, the calculated PDOS of TY, BCP and TY/BCP complex are presented. The PDOS as well as Fermi levels were calculated by using the Gauss Sum 2.2.5 program [18] at the B3LYP/SDD level of theory. As shown, the PDOS become more abundant near Fermi levels going from D to CT complexes. This strong interaction between TY and BCP may originate

from the hybridization between the TY and BCP as the projected density of states (PDOS) that corresponding to the TY and BCP shown in Figure 8. In fact, the TY can able to donate its electrons to the BCP due to its low ionization potentials with respect to BCP. The antibonding orbitals of OH group, above the Fermi energy at 2 eV Figure 8a, disappear in Figure 8c and this depicts the charge transfer from OH group to the phenyl ring of TY then to the BCP.

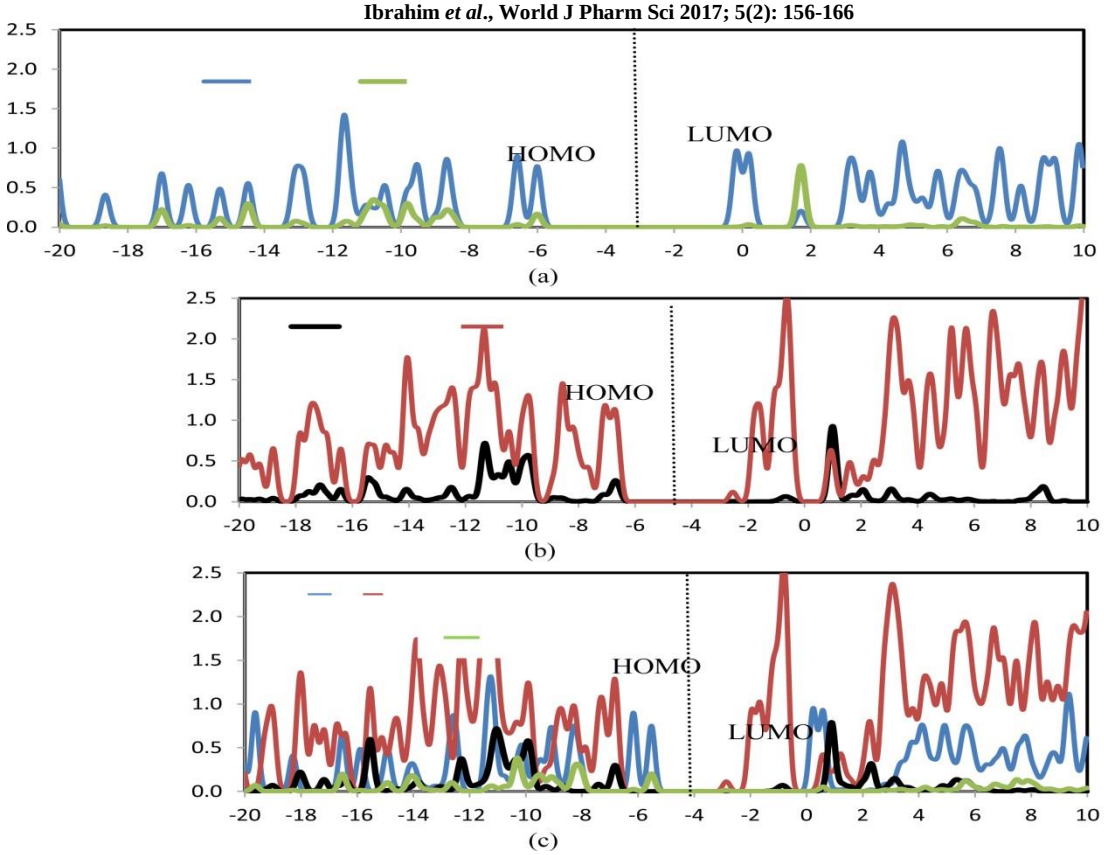


Figure 8: The partial density of states (PDOS) of (a) TY (b) BCP (c) TY/BCP complex , the Fermi level is indicated by a dotted line.

Polarisability and hyperpolarisability: In this study, the electronic dipole moment, molecular polarisability, anisotropy of polarisability and molecular first hyperpolarisability of the TY, BCP and TY/BCP complex are investigated. Polarisabilities and hyperpolarisabilities characterize the response of a system in an applied electric field. They determine the strength of molecular interactions as well as the cross sections of different scattering and collisionprocesses. Ditchfield et al [32-36] may also emphasise that the significance of the hyperpolarisability and the first hyperpolarisability of molecular systems is dependent on the efficiency of electronic communication between acceptor and the donor groups as that will be the key to intramolecular charge transfer.

Furthermore, it is well known that the higher values of molecular polarisability, hyperpolarisability and dipole moments are important for more active NLO performance. The polarisability and hyperpolarisability tensors (α_{xy}, α_{yy}, α_{xz}, α_{yz}, α_{zz} and β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz},β_{yyz}, β_{xzz}, β_{yzz}, β_{zzz}) can be obtained by finite field,

sum over states method and coupled perturbed HF method. The microscopic polarisability (P) induced in an isolated molecule under the applied electric field (E) of an incident electromagnetic wave can be expressed by the following equation:

$$P = \alpha E + \beta EE$$

where P and E are related to the tensor quantities α and β which are referred to as the polarisability $P$and first hyperpolarisability, respectively. Cinar et al [37] were known the mean polarisability are

$$a = 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

the anisotropy of polarisability is

$$\Delta\alpha = 1/\sqrt{2}\ [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\,\alpha_{xz}^2 + 6\,\alpha_{xy}^2 + 6\,\alpha_{yz}^2]^{1/2}$$

and the average value of the first hyperpolarisability is

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

or simply

$$\beta_{ii} = 1/5 \sum i(\beta_{iiz}\ \beta_{izi}\ \beta_{zii})\ (i \text{ from x to z})$$

The calculated parameters described above for TY, BCP and TY/BCP complex are given in Table 4 from which several facts emerge: (i) the larger polarisability a is assigned to TY/BCP complex and dominated by the term α_{xx}. The largest value of the average hyperpolarisability term β is assigned to TY/BCP complex and dominated by the term β_{xxx} for TY/BCP complex. All of the hyperpolarisability terms are significantly affected by forming the CT complex. The results also suggest that the formation of CT complex leads to more active NLO performance and stronger response to the external electric field. Moreover, the calculated energy levels of the TY (donor) relative to the BCP (acceptor), Figure 3, and the calculated red-shifted absorption bands under the effect of TY/BCP complex, Table-4, is attributed to increasing electron injection from the donor moiety to the acceptor moiety. This increase in electron injection induces the increase in NLO properties, such as polarisability and hyperpolarisability components, reported in Table 4 under the effect of CT complex.

Table 4: Polarizabilities (α) and hyperpolarizabilities (β) of the TY, BCP and TY/BCP complex calculated at the B3LYP/SDD level of theory.

	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	α	Δα
TY	142.24	-0.07	109.84	-0.0135	-0.0014	69.17	**107.08**	**63.42**
BCP	320.559	25.328	308.1	-3.899	4.037	255.35	**294.67**	**59.963**
TY/BCP complex	437.743	-7.408	454.09	9.3907	2.0368	615.426	**502.419**	**170.099**

	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{ii}
TY	-57.177	-67.164	-82.506	-31.436	-0.368	0.012	-0.248	9.13	-3.473	0.203	-0.248
BCP	-597.312	-132.03	400.653	-1448.5	-24.27	79.672	-68.482	-86	-38.353	184.59	55.10 1
TY/BCP complex	-1384.57	511.77	42.28	345.839	498.9	-91.15	31.091	-69.7	41.654	-34.271	297.4 31

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