

# Charge-transfer complex of Schiff-base derived from camphor with picric acid

Asmaa A. Ibrahim

Chemistry Department, Faculty of Science, Aswan University

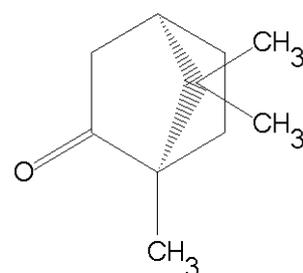
*Abstract-Schiff- base was obtained by condensation of camphor with 4-amino-phenol .The charge transfer complex of the Schiff base as a donor molecule with picric acid as acceptor molecule in methanol were estimated. Schiff-base compound and charge transfer complex were identified by elemental analysis, infrared spectra and UV-visible spectra.The physical parameters of the CT complex were calculated by applying the modified Benesi-Hildebrand equation for 1:1 CT complex. Computational study of the CT complex of Schiff base with picric acid.*

**Keywords:** Schiff base, physical parameters, HOMO-LUMO Binding energy.

## I. INTRODUCTION

Schiff base named after Hugo Schiff [1864] is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by a carbon – nitrogen double bond (C=N) with the nitrogen atom connected to an aryl or alkyl group, the Schiff base makes a stable aldimines or ketoimines [1]. A series of Schiff base ligands were synthesized from camphor [2]. Schiff base-camphorsulfonyl amide legends synthesized [3]. The study of the nature of interactions between donor and acceptor in a charge transfer complexes has attracted the attention of both theoretical and experimental [4,5] chemists worldwide. A study of the electrical properties of charge-transfer (CT) complexes of 2-aminopyrimidine and 2-aminopyrazine Schiff bases with nitrobenzene derivatives has been done [6]. The electrical conductivities of some Schiff bases and their charge transfer complexes with 2,4-dinitrophenol and picric acid as acidic acceptors indicate that they behave as semiconductors within the investigated range of temperature [7]. Charge-transfer complexes of quinaldine-arylidenschiff bases with fluoranil and 2,4-dinitrofluorobenzene have been investigated [8]. Charge-transfer (CT) complexes of pyrimidine Schiff bases, derived from condensation of 2-amino-pyrimidine and substituted benzaldehydes with some aromatic polynitro compounds were prepared and investigated [9]. Structural, spectral and thermal stability of charge-transfer (CT) complexes formed between the Schiff base as a donor with chloranilic acid, *p*-chloranil, tetracyanoquinodimethane or dichlorodicyano-benzoquinone as acceptors were reported [10]. The computational study on the non-covalent interactions of 1,3,5-trinitrobenzene with some indolyl Schiff's bases have been carried out by DFT [11]. The interactions between ellipticine and different hydrogen bond acceptor ions ( $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $AcO^-$ ) have

been investigated theoretically based upon density functional theory (DFT) method [12]. Camphor [13](ketone compound) is a waxy, white or transparent solid with the molecular formula. It is found in wood of the camphor laurel (*Cinnamomum camphora*). It is used for its scent, as an embalming fluid, for medicinal purposes. Modern uses include camphor as a plasticizer for nitrocellulose. Solid camphor releases fumes that form a rust-preventative coating, and is therefore stored in tool chests to protect tools against rust. Camphor crystals are also used to prevent damage to insect collections by other small insects (Scheme 1). The present study deals with the preparation of Schiff base, The solid complex (Sch) were synthesized and investigated by elemental analysis (CHN) and IR. The interaction of charge-transfer complex (Sch-Pa) includes the characterization of charge-transfer complex of Schiff base (Sch) as a donor with picric acid (Pa) as acceptor. Equilibrium constant ( $K_{CT}$ ), molar extinction coefficient ( $\epsilon_{CT}$ ), ionization potential ( $I_p$ ) oscillator strength ( $f$ ), the transition dipole moment ( $\mu$ ), ionization potential ( $I_p$ ) and standard free energy ( $\Delta G^\circ$ ) were evaluated. The energy gap between HOMO and LUMO calculated by using Density Functional Theory DFT method.



Scheme 1. Camphor

## II. EXPERIMENTAL

### A. Materials

Camphor (1,7,7-Trimethylbicyclo[2.2.1] heptan-2-one), Mol.wt.: 152.233, M.p.: 178.8°C,  $C_{10}H_{16}O$ , 4-aminophenol, Mol.wt.: 109.130, M.p.: 190°C,  $C_6H_7NO$  and picric acid (2,4,6-trinitrophenol), Mol.wt.: 229.11, M.p.: 123 °C,  $C_6H_3N_3O_7$ . The compounds were obtained from Germany. Solvents (Merck) were used throughout the investigation.

### B. Preparation methods

Preparation of Schiff-base (4-((E)-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)aminophenol)

Camphor (10 mmol, 1.52 g) was dissolved in 10 ml of methanol and to this solution was added 4-aminophenol (10 mmol, 1.09 g) in 10 ml of methanol and AcOH (1ml). The reaction mixture obtained was refluxed for 9 h. Upon cooling, the black crystalline powder Schiff- base (Scheme 2) was collected by filtration, washed with methanol and dried. Finally, the Schiff base was recrystallized from hot methanol to give pure black crystalline powder [14].

Elemental analysis for Schiff base were performed and the obtained results as follow:  $C_{16}H_{21}NO$ ; Mol.wt.:243.348; calc.: %C = 78.97; %H = 8.70; %N = 5.76. Found: %C = 78.01; %H = 8.99; %N = 5.22.

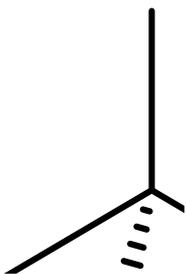
**Preparation of the charge transfer complex ((E)-N-((1R,4R),7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)-4-((2,4,6-trinitrophenyl)peroxy)aniline)**

Schiff-base were separately dissolved in 25 ml of methanol and mixed with 25ml of picric acid in mole ratio of 1:1. The mixture was stirred at room temperature for 4 h and the precipitated complex was then filtered off and dried under vacuum. Then, the precipitate was recrystallized from ethanol, and after one day, the complex was separated from the solvent and dried under a vacuum(Scheme 2).

Elemental analysis for CT complex (Sch-Pa) were performed and the obtained results as follow:  $C_{22}H_{24}N_4O_8$ ; Mol.wt.:472.458; Calc.: %C = 55.93; %H = 5.12; %N = 11.86. Found: %C = 55.71; %H = 5.43; %N = 11.52.

### C. Photometric titration

Photometric titration at 540 nm for the reaction between Schiff base (Sch) and picric acid (Pa) in methanol was carried out as follows: the concentration of Sch  $[D]_0$  was kept constant at  $0.4 \times 10^{-4}$  mol/L, whereas that of Pa  $[A]_0$  was changed over a wide range, from  $0.1 \times 10^{-4}$  –  $1.20 \times 10^{-4}$  mol/L. The donor-acceptor molar ratio (D:A) obtained in this case varied over the range from 1:0.25 - 1:3.00 (see Table 2). The absorbance peaks appeared in the spectra that assigned to the formed CT complex (Sch-Pa) were measured and plotted as a function of the ratio D: A, according to the known method (15).



**Scheme 2. Preparation of Schiff-base and charge transfer complex.**

### D. Molecular Modeling

The molecular modeling for the CT complex of Schiff base with picric acid was performed by using CS Chem3D Ultra, version 12(Cambridge Soft Corporation, Cambridge, MA, USA).

### E. Instruments

The elemental analyses of the carbon, hydrogen and nitrogen contents were performed by the microanalysis facility at Cairo University, Egypt.

The electronic absorption spectra of methanolic solutions of the donor, acceptor and resulting CTcomplex were recorded over a wavelength range of 200–800 nm using a Perkin-Elmer Lambda25UV/v is double- beam spectrophotometer at Aswan University,

The infrared spectra of the complex were recorded using KBr discs on Interspec 2020 FT- IR Spectrometer U.K at Cairo University, Egypt.

## III.RESULTS AND DISCUSSION

The electronic spectra of Schiff base display three absorption bands, the first band at 210 nm characterized by high absorbance, the band is due to the  $\pi-\pi^*$  transition of the aromatic moieties. The second band at 225 nm is due to the  $\pi-\pi^*$  transition of the N=CH of the azomethine group. The third band is the broad one and appeared at 395nm, composite band located at longer wavelength side is due to a charge transfer migration (CT), this band originates, most probably, from the camphor and phenyl ring as a donor to the azomethine asanacceptor (Fig.1).Mulliken [16,17] showed that the charge transfer interactions within a molecular complex consisting of an electron donor D and an electron acceptor A involved a resonance with a transfer of charge from D to A. The charge-transfer complex forming reactions are based on the concept that  $\pi$ -acceptor react with n-donor to form charge-transfer complex. The addition of picric acid to Schiff base solutions caused an immediate shift with a new characteristic band at 540 nm (Fig. 1) This compound was believed to be an intermediate molecular association complex which dissociates producing a picric acid radical anion. Newly detected bands in the near UV and visible spectrum (540, 360 and 230 nm) are observed immediately upon mixing solutions of Schiff base (Sch) and picric acid (Pa). The absorbance was contributed by the CT complexes, since both donor and acceptor alone did not absorb in this region. The electronic absorption spectra of the donor (Sch) with acceptor (Pa) are shown in Figure 1. The Sch:Pa molar ratio is 1:1 CT complex. The spectra revealed strong absorption bands attributed to the CT interaction. The spectrum of the Sch-Pa system shows one strong absorption band at 540 nm (red shifted) due to the formation of Sch-Pa CT complex. The photometric titration measurements based on the characteristic absorptions bands of the CT complexes are confirmed by the molar ratios of the studied complex see

in Figure 2, Table 1. The modified Benesi-Hildebrand equation [18,19] was used to determine the value of the equilibrium constant,  $K_{CT}$  ( $Lmol^{-1}$ ) and the extinction coefficient,  $\epsilon_{CT}$  ( $Lmol^{-1}cm^{-1}$ ) for the complex formed in solution (Table 2). This equation can be written as follows:

$[A]_o [D]_o / A = [A]_o + [D]_o / \epsilon_{CT} + 1 / K_{CT} \epsilon_{CT}$  Where  $[A]_o$  and  $[D]_o$  are the initial concentrations of acceptor and donor, respectively, while  $A$  is the absorbance at the mentioned CT bands. The data obtained throughout this calculation are given in Figure 3, Table 3. On plotting the values of  $[A]_o [D]_o / A$  values against the  $[A]_o + [D]_o$  values, a straight lines were obtained with a slope of  $1/\epsilon_{CT}$  and intercept of  $1/K\epsilon_{CT}$ . The oscillator strength ( $f$ ) which is a dimensionless quantity, used to express the transition probability of the CT-band [20] and the transition dipole moment ( $\mu$ ) of the CT complex [21]. The values of ( $f$ ) and ( $\mu$ ) are calculated by using the following equations:

$$f = 4.42 \times 10^{-9} (\epsilon_C \Delta\nu_{1/2})$$

$$\mu = 0.0958 (\epsilon_{CT} \Delta\nu_{1/2} / \nu_{CT})^{1/2}$$

where  $\Delta\nu_{1/2}$  is the half bandwidth of absorbance and  $\epsilon_{CT}$ ,  $\nu_{CT}$  are the extinction coefficient and wavenumber at maximum absorption peak of the CT complex, respectively. The resonance energy of the complex ( $R_N$ ) in the ground state is obtained from the theoretical equation derived by Brieglab (22):

$\epsilon_{CT} = 7.7 \times 10^{-4} / [h\nu_{CT} / [R_N] - 3.5]$  where  $\epsilon_{CT}$  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 energy of the  $\pi - \pi^*$  interaction ( $E_{CT}$ ) is calculated using the following equation [23]:

$$E_{CT} = 1243.667 / \lambda_{CT} \text{ nm}$$

The ionization potential of Sch is estimated from the CT energy of this complex with Pa by using equation derived by Aloisi and Pigantro [24]:

$I_{P(eV)} = 5.76 + 1.53 \times 10^{-4} \nu_{CT}$  The standard free energy changes of complexation ( $\Delta G^\circ$ ) were calculated from the equilibrium constant [25]:

$$\Delta G^\circ = -RT \ln K_{CT}$$

where  $\Delta G^\circ$  is the free energy change of the charge transfer complex ( $kCalmol^{-1}$ ),  $R$  is the gas constant ( $1.987 Cal mol^{-1} K$ ),  $T$  is the temperature in Kelvin and  $K_{CT}$  is the equilibrium constant of the complex ( $L mol^{-1}$ ) at  $25^\circ C$ . The data of  $f$ ,  $\mu$ ,  $I_P$ ,  $E_{CT}$  and  $\Delta G^\circ$  were represented in Table 3.

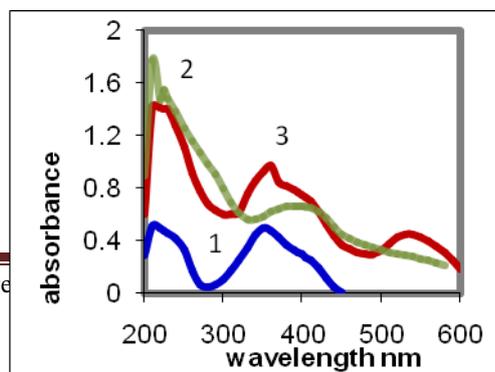


Fig. 1. Electronic absorption spectra of: 1-picric acid -2-Schiff base -3- CT complex.

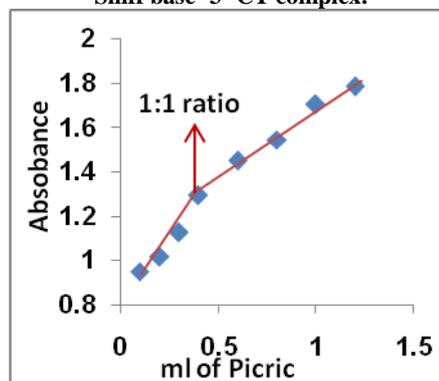


Fig. 2. Photometric titration curve of charge-transfer complex.

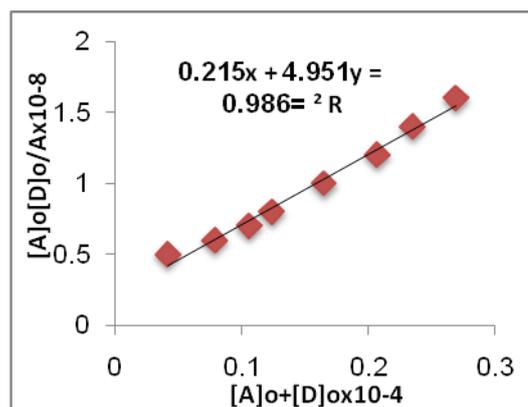


Fig. 3. The 1:1 Benesi-Hildebrand plot of charge-transfer complex.

Table 1. The electronic absorption spectral data for Schiff base- picric acid complex.

X ml of Pa	Sch:Pa	A at 540 nm
0.1	1:0.25	0.95
0.2	1:0.5	1.018
0.3	1:0.75	1.127
0.4	1:1	1.294
0.6	1:1.5	1.451
0.8	1:2	1.545
1	1:2.5	1.703
1.2	1:3	1.785

Table 2. The values  $[A]_o$ ,  $[D]_o$ ,  $[A]_o [D]_o / A$  and  $[A]_o + [D]_o$  for Schiff base- picric acid Complex.

$[D]_o$ x10 <sup>-4</sup>	$[A]_o$ x10 <sup>-4</sup>	Abs.	$[A]_o [D]_o / A$ x10 <sup>-8</sup>	$[A]_o + [D]_o$ x10 <sup>-4</sup>
0.1	0.25	0.95	0.262	0.35
0.2	0.5	1.018	0.980	0.7
0.3	0.75	1.127	2.000	1.05
0.4	1.0	1.294	3.060	1.4
0.6	1.5	1.451	6.180	2.1
0.8	2.0	1.545	10.360	2.8
1.0	2.5	1.703	15.780	3.5
1.2	3.0	1.785	21.420	4.2

0.1	0.95	0.042	0.5
0.2	1.018	0.079	0.6
0.3	1.127	0.106	0.7
0.4	1.294	0.124	0.8
0.6	1.451	0.165	1
0.8	1.545	0.207	1.2
1	1.703	0.235	1.4
1.2	1.785	0.269	1.6

$\nu(\text{C}=\text{N})$	-	1470 1449 1417	-	1474
$\nu_{\text{as}}(\text{NO}_2)$	-	-	1542	1335
$\nu_{\text{s}}(\text{NO}_2)$	-	-	1385	1236
$\nu\text{C}=\text{O}$	1744	-	-	-
H-bonding	-	-	-	3023 2959 2916

Table 3. Spectroscopic data of CT- complex.

$\lambda_{\text{CT}}$ nm	540
$K_{\text{CT}} \times 10^{-4}$ mol <sup>-1</sup>	22.9642
$\epsilon_{\text{CT}} \times 10^{-3}$ mol <sup>-1</sup> cm <sup>-1</sup>	2.019
$f$	9.182
$\mu$	10.263
$R_{\text{N}}$	0.044
$I_{\text{p}}$ ev	8.593
$E_{\text{CT}}$ K Cal mol <sup>-1</sup>	2.303
$-\Delta G$ K Cal mol <sup>-1</sup>	7309

The infrared spectra of the characterized bands of camphor, Schiff base, picric acid and CT complex of Schiff base with picric acid are shown in Figure 4. In the camphor, the stretching vibration of (C=O), (Me) and (C-H) group appeared at 1744, 2961 and 3469 cm<sup>-1</sup>, respectively. The IR spectra of Schiff base under study are shown in Fig.4 and Table 4, A broad stretching wavenumbers range between 3219- 2959cm<sup>-1</sup> which confirm OH group in the Schiff base. A strong to medium intensities bands are assigned to C=N, with stretching frequency range between 1513-1567 cm<sup>-1</sup>. The spectrum of charge transfer complex exhibit small shifts in frequency and changes in their band intensities. This result could be attributed to the expected changes in symmetry and electronic configurations upon the formation of the CT complex. The OH stretching vibration band in Schiff base was shifted in the CT complex. This shifted band is attributed to the stretching vibration of the intermolecular hydrogen bond. Hydrogen bond formed through the transfer of proton from the acidic center on the picric acid as acceptor to the basic center of the Schiff base (OH) based on acid-base theory [27,28].

Table 4. The infrared spectra of camphor, Schiff base, picric acid and CT complex.

Assignments	Cam	Sch	Pa	CT
$\nu\text{O-H}$	-	3219	3218	3341 3179

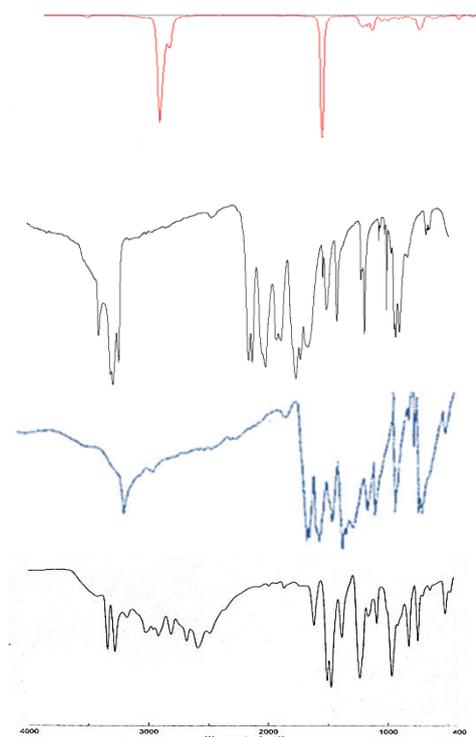
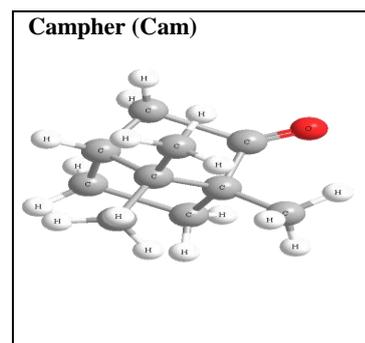


Fig.4. IR data for camphor, Schiff base, picric acid and CT complex.

The molecular structures of camphor, Schiff base, picric acid and charge transfer complex in the ground state were optimized (Figure 5). The HOMO, LUMO and the results of the energy gap values of CT complex were calculated (figure 6), which support the idea that the Schiff base act as donor due to high electron density while picric acid act as acceptor.

Fig 5. Picture of campher, Schiff base, picric acid and CT complex.



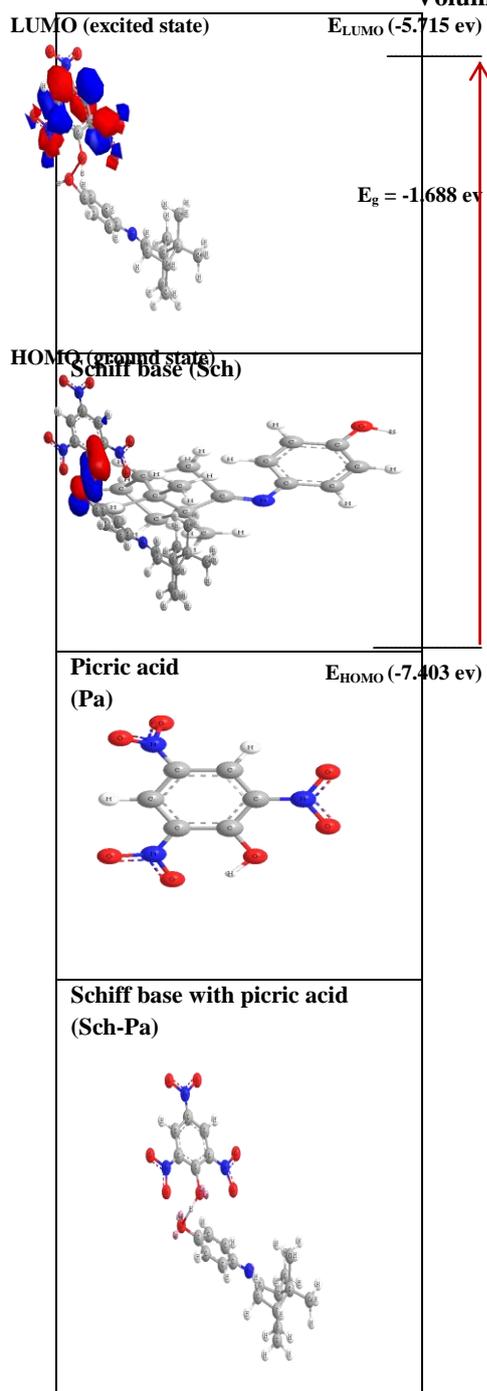


Fig.6.HOMO–LUMO energy gap of CT-complex

#### REFERENCES

[1] R.H. Holm, G.W. Everett and A. Chakravorty, "Metal Complexes of Schiff Bases and  $\beta$ -Ketoamines," *Progr. in Inorg. Chem.*, vol. 7, pp. 83-214, 1966.

[2] R. Boobalan, Ch. Chen and Lee, "Camphor-based Schiff base ligand," *Org. Biomol. Chem.*, vol. 10, pp. 1625, 2012.

[3] J. Sun, X. Pan, Zh. Dai and Ch. Zhu, "Synthesis of new Schiff base-camphor-sulfonyl amide ligands," *Tetrahedron: Asymmetry*, vol. 19, no. 21, 3, pp. 2451–2457, 2008.

[4] M. Nishihara, L. Christiani, A. Staykov, K. Sasaki, "Experimental and theoretical study of charge-transfer complex hybrid polyimide membranes," *J. Polymer Sci.*, vol. 52, pp. 4, 2014.

[5] S. Fomine, L. Fomina, T. Ogawa, "Charge transfer complexes between 4,4'-disubstituted diphenyl-diacetylenes: experimental and theoretical study," *J. Mol. Struct.*, vol. 540, no. 1–3, pp. 123–130, 2001.

[6] K.A. Darwish, M. Mounir, A.L. El-Ansary and H.B. Hassib, "Electrical properties of charge transfer complexes of 2-amino-pyrimidine and 2-aminopyrazine schiff bases with nitrobenzene derivatives," *Thermochim. Acta*, vol. 114, no. 2, pp. 265-271, 1987.

[7] A.M.A. Ibrahim, "Electrical and thermal behavior of some Schiff bases and their charge transfer complexes with acidic acceptors," *Thermochim. Acta*, vol. 197, no. 1, pp. 211-217, 1992.

[8] E. H. El-Mossalamy and S. A. Al-Thabaiti SA, "charge-transfer complexes of quinaldine-arylidenschiff bases with fluoranil and 2,4-dinitrofluorobenzene," *Heterocyclic communications*, vol. 10, pp. 2, 2004.

[9] Y. M. Issa, A. L. El Ansary, O.E. Sherif and H.B. Hassib, "Charge-transfer complexes of pyrimidine Schiff bases with aromatic nitro compounds," *Spectrochim Acta A.*, vol. 79, no. 3, pp. 513-21, 2011.

[10] M. S. Refat, M.Y. El-Sayed and A. A. Adam, "Structural, Electronic and Thermal Studies of Charge-Transfer Complexes from the Schiff Base," *Canadian Chem. Trans.*, vol. 2, no. 2, pp. 149-159, 2014.

[11] K.K. Srivastava, Sh. Srivastava, Md. T. Alam and Rituraj, "Quantum mechanical studies on charge transfer complex of some Indolyl Schiff bases with 1,3,5-trinitrobenzene," *EJAS J.*, vol. 1, no. 1, pp. 17-22, 2013.

[12] S. Paul, A. Mallick, T. Majumdar, "Computational study on the ion interaction of ellipticine," *Chemical Physics Letters*, vol. 634, pp. 29–36, 2015.

[13] J. C. Mann, J. B. Hobbs, D. V. Banthorpe and J. B. Harborne, "Natural products: their chemistry and biological significance". Harlow, Essex, England: Longman Scientific & Technical.

[14] V. M. Kolb, A. C. Kuffel, H. O. Spiwek and T. E. Janota, *J. Org. Chem.*, vol. 54, pp. 2771, 1989.

[15] D. A. Skoog, *Principle of Instrumental Analysis*, 3rd. Saunder College Publishing, New York, 1985 (Chapter 7).

[15] R.S. Mulliken, *J. Am. Chem. Soc.*, vol. 74, pp. 811, 1952.

[16] R.S. Mulliken, *J. Phys. Chem.* vol. 56, pp. 801, 1952.

[17] B. K. Seal, H. Sil and D.C. Mulcherjee, *Spectrochim. Acta*, 38A, pp. 289, 1982.

[18] H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, vol. 71, pp. 2703, 1949.

[19] H. Tsubomura and R. Lang, *J. Am. Chem. Soc.* vol. 86, pp. 3930, 1964.

[20] R. Rathone, S.V. Lindeman and J.K. Kochi, *J. Am. Chem. Soc.*, vol. 119, pp. 9393, 1997.

- [21] G. Briegleb and J. Czekalla, *Z. physikchem.* vol.24, pp.237, 1960.
- [22] G. Briegleb and Z. *Angew.Chem.*, vol. 72,pp.401,1960; G. Briegle, *Z.Angew.Chem.*, vol.76,pp.326,1964.
- [23] G.Aloisi, S.Pignataro, *J.Chem.Soc.FaradayTrans.* vol.69, pp.534, 1972.
- [24] A.N.Martin, J.Swarbrick and A.Cammarata, *Physical Pharmacy*, 3 ed., Philadelphia, PA: Lee and Febiger, 1969, pp. 344.
- [25] M.S.Refat, H.A. Saad and A.A. Adam," Proton transfer complexes based on some  $\pi$ -acceptors having acidic protons with 3-amino-6-[2-(2-thienyl) vinyl]-1, 2, 4-triazin-5 (4H)-one donor ,"*J. Mol. Str.*, vol.995, no. 1-3,pp.116,2011.
- [26] A.M.A. Adam,"Structural, thermal, morphological and biological studies of proton-transfer complexes formed from 4-aminoantpyrine with quinol and picric acid,"*Spectrochim. Acta A*, vol.104, pp.1-13, 2013.[28] A.M.A. Adam, "Synthesis, spectroscopic, thermal and antimicrobial investigations of charge-transfer complexes formed from the drug procaine hydrochloride with quinol, picric acid and TCNQ,"*J. Mol. Struct.*, vol.1030,pp.26-39,2012.