Synthesis and Spectral Characterization of Some New Aromatic Schiff Bases Derivated from 2,4-Dinitrophenylhydrazine

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Abstract

Four novel Schiff bases SB1 to SB4 as new aromatic compound not hydrolysed under ordinary conditions were synthesized in this study by condensation reactions between2,4-dinitrophenylhydrazine: firstly with 2,4,4`-trihydroxybenzophenone to give SB1, secondly with 4-hydroxybenzophenone to give SB2, thirdly with 4-dimethylaminobenzaldhyde to give SB3 and fourthly with 4-aminobenzaldehyde to give SB4. The molecular structures of these aromatic Schiff bases obtained were identified and characterized based on melting points, elemental analysis(CHN), FT-IR and UV-Visible spectra. The electronic absorption spectra of Schiff bases obtained were studied in the solvents of ethanol, DMF, water, chloroform, carbon tetrachloride and cyclohexane. The recorded absorption bands in ethanol solvent were assigned to corresponding electronic transitions were discussed. The absorption bands at 291 to 411 nm obtained in electronic spectra of the synthesized new aromatic Schiff bases were assigned to (π→π*) transition which originates from substituted benzophenone or benzaldehyde rings and directed along of molecule in Schiff bases. These transitions are assumed to represent the intramolecular charge-transfer complexes bands in which the substituted two moieties of benzophenone and benzaldehyde rings are the charge donors and the substituted phenylhydrazine ring is the charge acceptor. Also, the effect of polar, non-polar solvents on the electronic transitions of charge-transfer bands have measured and discussed.

The physical-spectroscopic parameters in molecular structural shapes of intra CT complexes molecules such as transition energies, molar extinction coefficients, molecular oscillate strength; transition molecular dipole moment and molecular resonance have been calculated and discussed.

Key word: Schiff base, charge-transfer complexes, FT-IR, CHN, UV-Visible

1. Introduction.

Schiff bases are an important species of organic compounds. Which where prepared in 1864 by a German chemist, Hugo Schiff, Nobel prize winner [1]. These compounds are produced from condensation of primary amines or hydrazine compounds with carbonyl compounds such as aldehydes or ketones. Structurally, Schiff base which also known as azomethine or imine compound in addition to hydrazone class is an analogue of aldehyde or ketone of aldehyde or ketone in which the carbonyl group will be replaced by an imine group (-CH=N- or C=N-) [2,3]. The preparation of Schiff bases are reversible reactions and take place under acid catalysis or by direct fusion [4-6]. In recent years, Schiff bases have been shown to a wide range of biological activity, including antibacterial, antifungal, antiviral, anticancer, antimonial, antiprotiferate, anti-inflammatory, antipyretic and Biocidal properties [7-11]. The azomethine and hydrazone group (-CH=N-NH- or C=N-NH-) in Schiff bases have been shown to be decisive to their biological activities [12,13]. Schiff bases are a set of organic intermediates which are used also in the synthesis and chemical analysis. They are used in the production of the drugs and agrochemical industry. The transition elements and the other certain metallo-elements are known to from aromatic Schiff bases complexes [14,15]. Aromatic Schiff bases behave as flexi-dentate ligands and ordinarily coordinate through nitrogen atom of imine group, oxygen atom of the de-pronated phenolic group and other donor atoms [16]. Charge-transfer complexes of Schiff bases are great importance in chemical interaction, including intramolecular charge-transfer complexes, biochemical and bioelectrochemical energy transfer processes, biological systems, drugs- acceptors binding mechanisms and drugs analysis [17-20]. Moreover, charge-transfer complexations are of great importance in many applications and fields, such as electrical conductivities of materials, optical activities, surface chemistry, solar energy storage, semiconductors and investigations of redox processes [21-23].based on this, we decided preparation new aromatic Schiff bases are not hydrolysed under ordinary condition and derived from 2,4,4`-trihydroxybenzophenone, p-hydroxybenzophenone, p-dimethylaminobenzaldehyde and p-aminobenzaldehyde with 2,4-dinitrophenylhydrazine may fit-those purpose, then identification of molecular structures by elemental analysis and spectra of IR, and UV-Visible. The study also includes explanation of electronic transition, determination of the physical spectroscopic parameters.

2. Experimental

2.1 Chemical Materials

All of the chemicals used were of high purity degree and were used without purification. The solvents of ethanol and methanol were used of Analar grade and supplied by Fluka Company, while the solvents of cyclohexane, carbon, tetrachloride, chloroform and dimethylformamide were of Spectroscopic grade which were supplied by BDH Company. Organic compounds of 4-hydroxybenzophenone (98% purity grade) and 2,4-dinitrophenylhydrazine (99% purity grade) were supplied by Merck Company, 4-Aminobenzaldehyde and 4-dimethylaminobenzaldehyde (99% purity grade) were supplied by BDH Company, while 2,4,4`-trihydroxybenzophenone (98% purity grade) was supplied by INC Company.

2.2 Instruments

Melting points were recorded using Gallenkamp melting points apparatus which measures the extent to 280˚C. The elemental analyses of the carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400 (USA). FT-IR spectra data were obtained by Shimadzu-8400S- FT-IR Spectrophotometer in the wave number range of 4000-400 cm^{-1} which included in KBr discs. The electronic absorption spectra were recorded in different solvents and media over wavelength range of 190-900nm by the Varian DMS 100 UV-Visible double-beam spectrophotometer which linked thermostaticall controlled unit. The instrument was equipped with a quartz cell of path length 1.0cm.

2.3 Synthesis of Schiff Bases.

Four aromatic Schiff bases were prepared as follows: (1) Schiff bases SB1 was prepared by mixing equimolar amounts (0.05 mol) of 2,4-dinitrophenylhydrazine (0.9909gm, m.p. 197-200 ˚C) and 2,4,4`-trihydroxybenzophenone (0.1512gm, m.p. 196-197˚C), both dissolved in 25 ml ethanol solvent then added (2-3) drops of concentrated HCl (36%). The reaction mixture was heated under back reflux for 8 hour, after cooling maroon crystals product was separated, then filtered. The solid product was crystallized by ethanol, then dried. Melting point of SB1 was recorded higher than 280˚C. Schiff bases SB2 prepared by mixing equimolar amounts of 2,4-dinitrophenylhydrazine (0.9907gm) and 4-hydroxybenzophenone (0.9911gm, m.p. 110-112˚C), both dissolved in 25 ml ethanol solvent and added (2-3) drops of concentrated HCl (36%). The reaction mixture heated under back reflux for two hour, after cooling orange precipitate was separated, then filtered. The solid precipitate was recrystallized by ethanol, and then dried. Melting point of SB2 was recorded 218-220˚C. Schiff base SB3 prepared by mixing equimolar amounts ofand 2,4-dinitrophenylhydrazine (0.991gm) and 4-dimethylaminobenzaldehyde (0.736gm, m.p. 73-75˚C), both dissolved in 30 ml methanol solvent and then added (3) drops nearly of concentrated HCl (36%). The reaction mixture heated under back reflux for 1 hour, after cooling black precipitate was separated in solution, and then filtered. The black precipitate was crystallized by methanol, then dried. Melting point of SB3 was recorded than 235-237˚C. Schiff bases SB4 was prepared by mixing equimolar amounts of 2,4-dinitrophenylhydrazine (0.9911gm) and 4-amiobezaldehyde (0.6061 gm, m.p. 165-168˚C), both dissolved in 30 ml methanol solvent and added (3) drops of concentrated HCl (36%). The reaction mixture heated under back reflux for 2 hour, after cooling black brown precipitate was separated in solution, then filtered and washed by cyclohexane.. The black brown precipitate was recrystallized by methanol, and then dried. Melting point of SB4 was recorded higher than 184-186˚C.The molecular structures of these Schiff bases characterized and identified by their melting points, elemental analysis (CHN) and spectra of FT-IR and UV-Visible.

2.4 Preparation of Samples Solutions.

Standard solutions were prepared for spectral measurements of the materials that included in this study from 2,4-dinitrophenylhydrazine, aromatic carbonyls derivatives and the prepared new aromatic Schiff bases in gravimetric method. We weight the required amount from solute substance in certain volume of proper solvent in volumetric flask to prepare standard stock solution, than prepare different concentrations for spectral measurement in UV-Visible spectroscopy in dilution method from standard solution.

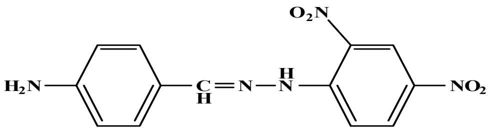
3. Results and Discussion

3.1 Chemistry and Characterization.

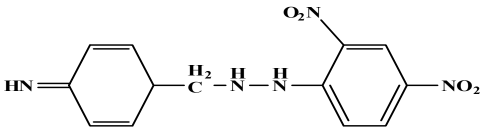
New Schiff bases have been synthesized from the condensation 2,4-dinitrophenylhydrazine with2,4,4`-trihydroxybenzophenone,4–hydroxybenzophenone, 4-dimethylaminobenzaldehyde and 4-aminobenzaldehyde(Scheme(1)). They are stable at room temperature and commonly soluble in methanol, ethanol, water and DMF. The elemental analysis (CHN), yield percentage physical state, color and melting point of these Schiff bases SB1-SB4 are presented in Table(1).

3.2 Melting Points.

From melting points in Table(1), it is expected that there in Schiff base SB1 both inter- and intramolecular hydrogen bonds because of three hydroxyl groups in ortho- and para- positions on the phenyl groups. It is known that intermolecular hydrogen bonding increase the melting point of the organic compounds [24]. Also, the melting point of the Schiff bases SB1, SB2 and SB3 , >280, 218 and 235°C respectively, are higher than Schiff base SB4. However, melting point of Schiff base SB4 is lower (184°C) than Schiff base SB1which includes intra- and intermolecular hydrogen bonding. Some substituted aromatic Schiff bases exhibit the ketamine tautomeric shapes and their common feature which is the presence of the substituted hydroxyl or amino group on the aromatic ring [24]. The low melting point of Schiff base SB4 may be explained by (I) and (II) tautomerism shapes as shown below:



(I)



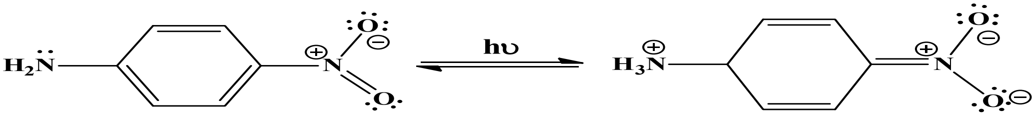
(II)

3.3 FT-Infrared Spectra.

The relevantFT-IR spectral absorption bands that can provide the identification structural evidences as FT-IR spectral data (from KBr disks) of the synthesized new aromatic Schiff bases are shown in Table(2), which are recorded as characteristic bands wave numbers (cm^{-1}) data from FT-IR spectra of the Figures 1to 4. The FT-IR spectra of these Schiff bases show very strong or strong intensity of absorption bands at 1607-1635cm^{-1} assigned to stretching vibration of azomethine bond ($\upsilon_{C=N}$) which are as follows: 1614, 1014, 1607 and 1635cm^{-1} attributable to SB1to SB4 respectively[24, 25]. The presence of aromatic rings has been identified by their characteristic aromatic ring vibration at (1400-1500), (1050-1100) and (700-900) cm^{-1} regions, including the bending vibration bands of C-N bond (γ_{C-N}) which are (1055, 1097), (1051, 1086, 1078 and 1018 cm^{-1} assigned to SB1to SB4 respectively. The stretching vibration bands at 1275cm^{-1} attributable to vibration of C-O bond (υ_{C-O})in SB1and SB2 [24-26]. The absence of absorption bands characteristic of C=O bond ($\upsilon_{C=O}$) and primary amine (υ_{N-H}) confirm the formation of the synthesized new aromatic Schiff bases framework, accept N-H bond in SB4. The stretching vibration bands of C-H bond in (υ_{C-H}) IN –CH=N- group appear at 3090 and 2966cm^{-1} for SB3 and SB4 respectively, while stretching vibration band of NO_2 group appear at 1512, 1510, 1512 and 1529cm^{-1} as strong intensities in SB1, SB2, SB3 and SB4 spectra, respectively. The strong intensities absorption bands at 1337, 1335, 1325 and 1350cm^{-1} attributable to the stretching vibration bands of N-N bond (υ_{N-N}). The band at 3070cm-1in the spectrum SB1 (Figure1) shows the OH….N intramolecular hydrogen bond between proton of hydroxyl group in ortho- position and nitrogen atom [24, 25]. Also,the broad band at 3454 and 3421cm^{-1} attributable to hydroxyl group bonded by intermolecular hydrogen bonding in SB1 and SB2 respectively, while the broad band at 3138cm^{-1} attributable to primary amine bonded by intermolecular hydrogen bonding. The stretching vibration band with strong intensity at 3277cm^{-1} is attributable to C-H bond of methyl group in SB3 in Figure (3) [25, 26].

3.4 Electronic Spectra and Their Explanation.

Figure (5) to (8) represent the electronic spectra of the synthesized new aromatic Schiff bases which contain substituted phenyl rings with hydroxyl, dimethylamino, amino or nitro and azomethine groups. Table (3) shows all the absorption bands of electronic transition. These absorption bands can be explained as follows: The absorption band at 198, 197, 201 and 201nm in the electronic spectra of SB1 to SB4 respectively, all these represent the local excitations ($\pi \rightarrow \pi^*$) transitions of the substituted phenyl rings, which correspond the transition ($^1A_{1g} \rightarrow {}^1E_{1u}$) at 184nm of benzene ring [6, 25, 27], and support that in this work absorption intensities of these bands decrease for their values compared with the intensity value at 184nm (6000 m^2.mol^{-1}) of benzene ring [25]. This can be explained due to azomethine and nitro groups presence which do as electron-withdrawing groups and cause an inductive effect in each of SB1 to SB4, hence decreases the transition intensities on the aromatic substituted phenyl rings [6, 25]. The absorption bands 207, 217 and 222 nm all shoulders in electronic spectra of SB1, SB2 and SB4 respectively represent the local excitations ($\pi\rightarrow\pi^*$) transitions of substituted phenyl rings which correspond to the electronic transition ($^1A_{1g} \rightarrow {}^1B_{1u}$) at 203nm of benzene ring [25]. We think that the absorption bands for this transition in SB3 did not appears because its intensity can be submerged under B-band or /and K-band [25, 27]. The absorption bands at 224, 244, 241 and 242nm as shoulder in the electronic spectra of Schiff bases SB1 to SB4 respectively, represent the local excitations ($\pi \rightarrow \pi^*$) transitions of substituted phenyl rings which correspond the electronic transition ($^1A_{1g} \rightarrow {}^1B_{2u}$) at 256nm of benzene molecule [6, 25], while the bands at (298, 293), (291, 385), (314, 411) and (320, 406) nm in electronic spectra of SB1 to SB4 respectively, all these bands represent ($\pi\rightarrow \pi^*$) transitions which are originated from substituted groups as electron-donating groups on carbonylic ring, and extended over the whole Schiff bases molecule to substitute to nitro groups as electron-withdrawing groups on the hydrazine phenyl rings. The presence of one or more hydroxyl group in the ortho or para position or both and dimethylamino or amino group at the para position in the Schiff base molecule enhances such transition [25, 27]. Theses absorption bands can suggest there is due to intramolecular charge transfer effect of the formed molecular chromophore which includes electron donor part and electron acceptor part within the same molecule of Schiff base. These intracharge-transfer states are similar to the intracharge-transfer in p-nitroaniline molecule which absorbs the light at 376nm as follows [27, 28]:



Molecular chromophore (CTC) which absorbs the at 376 nm.

3.5 Spectroscopic-Physical Parameters of Infra CT Complexes.

The spectroscopic and physical parameters of intracharge-transfer complexes in SB1 to SB4, such as transition energy ($h\upsilon_{CT}$), molar extinction coefficient (ε_{CT}),the molecular oscillate strength (f_{CT}), transition molecular dipole moment(μ_{CT}), resonance energy (E_R) in the molecular structure shape of intracharge-transfer complex molecule. These parameters were calculated and inserted in Table (4) for SB1 to SB4 dissolved in ethanol solvent at 20^{o}C. All values have been appointed by charge-transfer band with least energy in the electronic spectra of SB1-SB4 as shown in the figures (5) to (8). The transition energy of the ($\pi \rightarrow \pi^*$)

transition at intracharge-transfer band was calculated using the conversion factor between the energy by electron volt unit (eV) and wavelength (λ_{CT}) by nanometer (nm) as shown in equation(1).

$$h\upsilon_{CT}(eV) = 1240.8\ (nm.\ eV)\ /\ \lambda_{max}(nm) \quad (1)$$

The molecular oscillate strength at excited state of the intracharge-transfer complex molecule has been estimated using approximate formula by equation (2) [29 and 30].

$$f_{CT} = 4.319 \times 10^{-9}\ \varepsilon_{CT}\ .\ \Delta\bar{\upsilon}_{1/2} \quad (2)$$

Where $\Delta\bar{\upsilon}_{1/2}$ is the half band width and ε_{CT} is the extinction coefficient. The value ($4.319*10^{-9}$) in equation (1) is number without units. When units of ε_{CT} and $\Delta\bar{\upsilon}_{1/2}$ are ($l.mol^{-1}.cm^{-1}$) and (cm^{-1}) respectively, the units of f_{CT} in equation (2) becomes ($l.mol^{-1}.cm^{-2}$). The molecular oscillator strength represents quantitative measurement of a dimensionless used to express the electronic charge-transfer probability from HOMO of electron donor part to LUMO of electron acceptor part within the molecular structure of intracharge-transfer complex molecule [31, 32].The transition molecular dipole moment at excited state of the intracharge-transfer complex molecule has been calculated by the equation (3)

Where $\bar{\upsilon}_{CT}$ is the wave number of charge-transfer band. The value $9.582*10^{-2}$ is constant by unit (Debye. $l^{1/2}$. $mol^{1/2}$. $cm^{1/2}$). When the values units of ε_{CT} ($l.cm^{-1}.mol^{-1}$), $\bar{\upsilon}_{CT}$ (cm^{-1}) and $\Delta\bar{\upsilon}_{1/2}$ (cm^{-1}),the unit of μ_{CT}becomes(Debye).value of transition molecular dipole moment reflects quantitative measurement for the intracharge-transfer overlap range and the direction which gives the polarization of the transition, in addition to determine how the molecular system will interact with an electromagnetic wave, while the square of the value (μ^2_{CT}) reflects the strength of the interaction due to the distribution of charge within the structure of molecular chromophore [27, 28]. The molecular resonance energy at ground state of the intramolecular charge-transfer complex molecule in has been estimated by the theoretical equation (4) [33].

$$E_R = \frac{h\,\upsilon_{CT}\ .\ \varepsilon_{CT}}{7.7x\ 10^{-4}\ + (\ 3.5\ \varepsilon_{CT}\ )} \quad (4)$$

Where value ($7.7*10^{-4}$) is the same unit of ε_{CT}, while the value (3.5) is number without units. When unit of ($h\upsilon_{CT}$) is electron volt, the unit of E_R in equation (4) becomes (eV). Molecular resonance energy valuereflects obviously as contributing factor to stability of the molecular chromophores of intramolecular charge-transfer complex molecule [28]. Returning to Table (4), the values of the (μ_{CT}) and (E_R) reflect the relative stability of intracharge-transfer complexes molecules and these values increase with increasing the stability of the molecular chromophores shapes for Schiff bases molecules from SB1to SB2, as well as from SB3 to SB4 except molecular resonance energy (E_R) value of SB3 is less. The stability of Schiff base SB3 is less compared with Schiff base SB4 due to the steric hindrance effect of dimethyl groups with unshared-pair of electrons on nitrogen atom [25]. The results of the($h\upsilon_{CT}$) and (ε_{CT})agree well with the values of (E_R) and (μ_{CT}).This agreement support the explanation provided. The relative high values of (f_{CT}) and (μ_{CT}) for intramolecular charge-transfer complexes in Schiff bases SB1,SB2 and SB4 suggested the formation of inner sphere complexes ($D^{+}\rightarrow A^{-}$) in the excited state, while lower values for SB3 suggested the formation of outer sphere complex ($D^{+\delta}\rightarrow A^{-\delta}$) in excited state [34]. Scheme (3) shows molecular structures of intramolecular charge-transfer complexes of SB1 to SB4, which can be responsible for light absorption, and the values of physical parameters (f_{CT}, μ_{CT}, E_R).

3.6 Effect of Solvent Polarity on the Electronic Transitions

Table (5) shows nonpolar solvent effect (cyclohexane, carbon tetrachloride and chloroform) on absorption bands in electronic spectra of SB1-SB4, Table (6) shows polar solvent effect (ethanol, dimethylformamide and water). Clearly, the data seem that the polar and nonpolar solvents did not affect the absorption band at 193-263nm in the electronic spectra of SB1 to SB4, but there is marked effect on the longer wavelength absorption bands than 285 nm. Table (7) shows such effects and Figures (9) to (12) illustrate that the red shift ($\Delta\bar{\upsilon}$) in λ_{max} for longest wavelength absorption band of SB1-SB4. The red shift increases rapidly with increasing dielectric constant of the solvent until the value (50) nearly for SB1, (30) for SB2, (10) for SB3, and (24.33) for SB4, after that the increase becomes gradual to the value of water 76.5. The increase of red shift ($\Delta\bar{\upsilon}$) with dielectric constant of solvent may explained as follows: After absorption light, the excited state of Schiff base molecule becomes more polarthan its ground state, therefore the polar solvent stabilizes the excited state by connecting dipole of Schiff base molecule with positive and negative ends of the solvent molecules. The more delocalization of the charge in the excited state of Schiff base molecule, higher increase of red shift ($\Delta\bar{\upsilon}$) with dielectric constant occurs. This effect is very clear in the all cases of SB1-SB4.In these molecules there are hydroxyl, amino and dimethylamino groups which increase the delocalization of the charge in Schiff base molecule and leading to higher values of red Shift.Scheme(4) shows excited molecular shapes of intramolecular charge-transfer complexes and their CT bands in different solvents.

4. Conclusion

In recent years, considerable attentions has been devoted to the formation stable intra- and intermolecular charge-transfer complexes which consist within aromatic Schiff bases as drugs, biological activity compounds or semiconductors, in addition to numerous of other important applications. This interest stems from significant physical and chemical properties of these compounds. Results of study reported in this work are concerned with the preparation of four new aromatic Schiff bases not hydrolysed under ordinary condition and their structures were identifiedand characterized by melting points measurement, elemental analysis and FT-IR spectra in addition to detailed study using UV-Visible spectra measurement of these new aromatic Schiff bases charge-transfer complexes formed within their intramolecules.

It is observed from research data in this study, existence of intra CT complexes within the molecular shapes of these Schiff bases. The electronic transitions of intramolecular charge-transfer complexes are ($\pi \rightarrow \pi^*$) transitions and direction of these transition originates from electron-donating group ($-OH$, $-NH_2$, $-N(CH_3)_2$) and extended over the whole molecule to nitro groups in these aromatic Schiff bases molecules.

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Table(1): Physical characterization and elemental analysis CHN data of new Schiff bases SB1 – SB4.

Schiff base	formula and M.wt /g.mol^{-1}	Physical state and (Color)	% Yield	(m.p / °C)	CHN Elements analysis (Calculated)		
					%C	%H	%N
SB₁	$C_{19}H_{14}N_4O_7$ 410.36	Crystals (maroon)	87	(>280)	55.56 (55.61)	3.35 (3.41)	13.70 (13.66)
SB₂	$C_{19}H_{14}N_4O_5$ 378.36	Crystals (orange)	85	(218–220)	60.38 (60.32)	3.65 (3.70)	14.75 (14.81)
SB₃	$C_{15}H_{15}N_5O_4$ 329.33	Crystals (black)	76	(235–237)	54.64 (54.71)	4.50 (4.56)	21.35 (21.28)
SB4	$C_{13}H_{11}N_5O_4$ 301.28	Crystal (black brown)	91	(184–186)	51.69 (51.83)	3.58 (3.65)	22.99 (23.26)

Table (2): Characterization infrared band frequencies (cm^{-1}) data for prepared Schiff bases (SB1 - SB4).

Schiff base	υ(O-H), υ(=CH)*, υ(N-H)**,υ(CH)***	υ(C=N)	ɤ(C-N) with ring	υ(NO₂)	ɤ(N-N)	υ(C-O) with ring	Aromatic ring vibration	H-bonding in the IR spectra
SB1	3485s. 3454 br.m.bonded. 3070 br.m.bonded.	1614vs.	1055m. 1097m.	1512s.	1337s.	1275s.	702m. 743s. 833s. 866s. 919s. 962s. 1418s. 1458w.	Intra and inter H-bonding
SB2	3477s. 3421br.m. bonded.	1614vs.	1051w. 1086s.	1510s.	1335s.	1275s.	700s. 743m. 779m. 831s. 918m. 966w. 1420s.	Inter H-bonding
SB3	3090 m. * 3277 ***	1607vs.	1078w.	1512s.	1325s.	-------	708m. 743s. 820s. 903w. 926m. 946s. 1414s. 1447m.	--------
SB4	3308 vs. * 3138 br.s.bonded** 2966w.	1636s .	1018m.	1530s .	1350s .	-------	837s. 995m. 1450s.	Inter H-bonding

υ: streching vib. , ɤ: bending vib. , br. : broad S. : Strong, m. : medium, vs..: very strong.

Table (3): Electronic spectra bands data of the prepared aromatic Schiff bases in ethanol solvents at temperature 20°C.

Aromatic Schiff base	$\lambda_{max / nm}$ (Ɛ / m^2 . mol^{-1})			
SB1	198 (3620 ± 90) sh. 207(3250±70)	sh.244(1750± 60)	sh.298(910±30)	395 (2190±40)
SB2	197 (3880 ± 100) sh.217 (2480±50)	sh.244(1890±70)	sh. 291(920±40)	385 (2830 ± 80)
SB3	201 (430 ± 30)	sh.241(120±10)	314(120±5)	411 (220 ± 10)
SB4	200 (3020 ± 110) sh.222 (2360±90)	sh.242 (1790±60)	sh.330(1360±20)	406 (2490 ± 30)

λ_{max}: wavelength of absorption maximum, Ɛ: Extinction coefficient and sh. : shoulder.

Table (4): The values of transition energy, oscillate strength and values of transition dipole moment of intramolecular CT complexes for the synthesized aromatic Schiff bases SB1- SB4 in ethanol solvent and temperature 20ºC.

Aromatic Schiff bases	λ_{max}/nm	$h\upsilon_{CT}$/ eV	ε_{CT} / $dm^3.mol^{-1}.cm^{-1}$	$\Delta\bar{\upsilon}_{½}$/ cm^{-1}	f_{CT}/(cm. $molecule^{-1}*10^{22}$)	μ_{CT}/ Debye	E_R/ eV
SB1	395	3.141	21923	7207	1.134	7.570	0.897
SB2	385	3.223	28323	6156	1.251	7.851	0.921
SB3	411	3.019	2223	8143	0.130	2.614	0.863
SB4	406	3.056	24852	6956	1.241	8.029	0.873

Table (5):The non-polar solvents affect data on the electronictransitions in temperature 20^0C.

Schiff base	λ_{max} / nm ($\mathcal{E}$ / m^2. mol^{-1})		
	Cyclohexane	Carbon tetrachloride	Chloroform
SB1	389 *	257 (1410 ± 30) sh. 298 (830 ± 20) 390 (2230 ± 50)	sh. 251 * sh. 301 391
SB2	377 *	255 (1730 ± 40) sh. 289 (610 ± 20) 378 (3380 ± 60)	sh. 255 (1640 ±30) sh. 290 (820 ± 20) 380 (2390 ± 50)
SB3	sh. 196 (630 ± 30) 206(680 ± 30) 235 (840 ± 40) sh. 251(740 ± 30) 309(660 ± 20) sh. 321(630 ± 10) 407(1040 ± 50)	246 (160 ± 5) 263 (130 ± 5) 312 (190 ± 10) 408 (400 ± 10)	sh. 257(440 ± 10) 313 (540 ± 20) 409 (1790 ± 50)
SB4	390 *	257(1400 ± 40) sh.328 (1310 ± 30) 391(2810 ± 60)	sh. 253 * sh. 329 392

λ_{max}: Wavelength of absorption maximum.

***: Filtrate of saturated solution or not quantity dissolved.**

Table (6): The polar solvents affect data on the electronic transitions in temperature 20^{0}C.

Schiff base	λ_{max} / nm ($\mathcal{E}$ / m^2. mol^{-1})		
	Ethanol	DMF	Water
SB1	198(3620 ± 90) sh. 207(3250±70) sh.244(1750±60) sh. 298 (910±30) 395 (2150±40)	190 (4470± 80) sh.240(2480±50) 320(1480 ± 40) 405 (2420 ±60)	221(880±30) sh.257(760±20) 329(750±20) 420(880±30)
SB2	197(338 ±100) sh.217 (2480±50) sh.244 (1890±70) sh. 291(920±40) 385 (2830±80)	196(9600±100) sh.219(5050±80) sh.244(4050 ±60) 296(227 ±20) 386(5050 ±70)	sh.195(2290±60) 220(1630±20) sh.246(153±50) sh.299(780±40) 389(1930±50)
SB3	201 (430 ± 30) sh.241(120 ± 10) 314 (120 ± 5) 411 (220 ± 10)	193(1280±40) 219(1800±60) sh.244(440±20) sh.307(500±20) b 333 (550 ±20) 413 (340 ±10)	195 a sh.217 251 sh. 309 334 417
SB4	200 (3020 ± 110) sh.222(2360±90) sh. 242(1790±60) sh.330(1360±20) 406 (2490 ± 30)	196 (4970±90) sh.225(3000±50 b 257(2240±40) sh.333(2110±40) 408(3540±70)	195(1560±60) 225(1410±30) 261(1260±20) sh.341(1420±30) 413 (1650±50)

a: Not quantity dissolved.
b:not clear-cut shoulder nearly.

Table (7): Variation of red shift (Δῡ) with dielectric constant of the solvent (ε*) for highest wavelength absorption band in different solvent at temperature 20°C.

Solvent	ε^*	SB1			SB2			SB3			SB4		
		λ_{CT}	$\bar{\upsilon}_{CT}$	$\Delta\bar{\upsilon}_{CT}$	λ_{CT}	$\bar{\upsilon}_{CT}$	$\Delta\bar{\upsilon}_{CT}$	λ_{CT}	$\bar{\upsilon}_{CT}$	$\Delta\bar{\upsilon}_{CT}$	λ_{CT}	$\bar{\upsilon}_{CT}$	$\Delta\bar{\upsilon}_{CT}$
CycloC_6H_{12}	2.023	389	25710	000	377	26530	000	407	24570	000	390	25640	000
CCl_4	2.238	390	25640	70	378	26460	70	408	24510	60	391	25580	60
$CHCl_3$	4.720	391	25580	130	380	26320	210	409	24450	120	392	25510	130
C_2H_5OH	24.33	395	25320	390	385	25970	560	411	24330	240	406	24630	1010
$(CH_3)_2NCHO$	36.71	405	24700	1010	386	25910	620	413	24210	360	408	24510	1130
H_2O	78.54	420	23810	1900	389	25710	820	417	23980	590	413	24210	1430

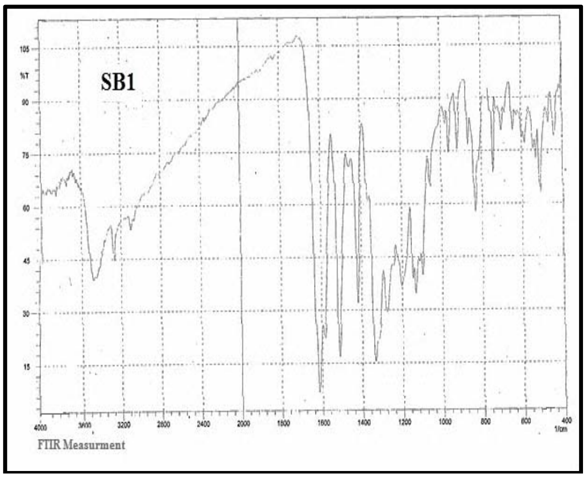


Figure (1): FT-IR spectrum of Schiff base SB1.

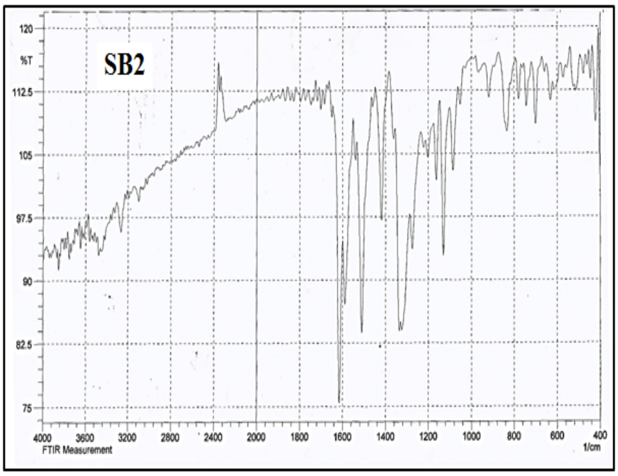


Figure (2): FT-IR spectrum of Schiff base SB2.

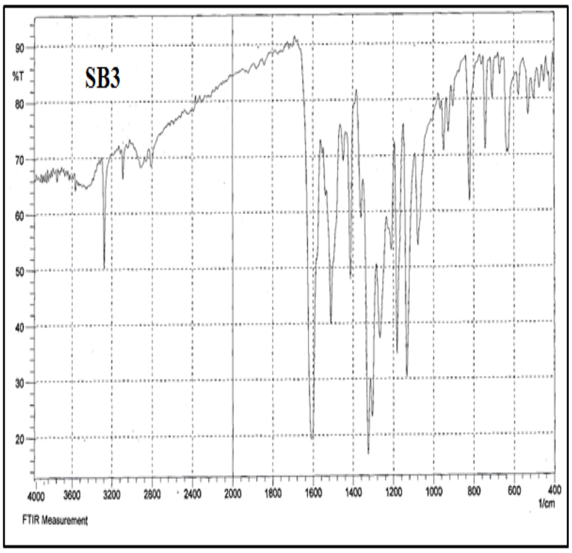


Figure (3): FT-IR spectrum of Schiff base SB3.

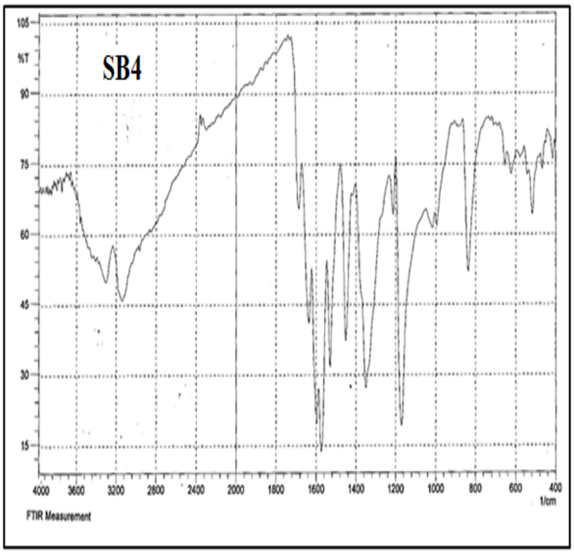


Figure (4): FT-IR spectrum of Schiff base SB4.

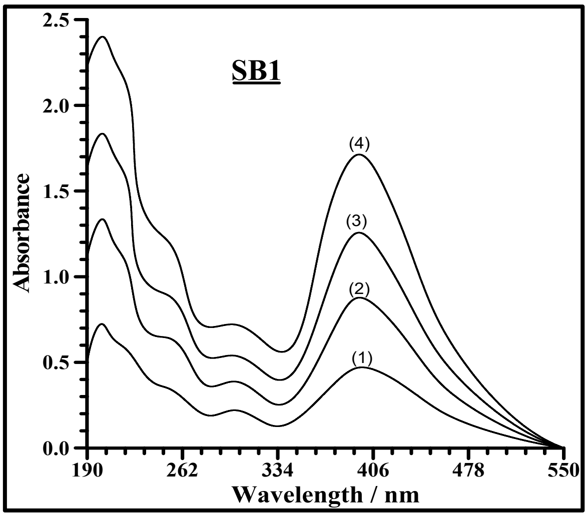


Figure (5): Electronic spectrum of SB1 in ethanol [(1) $1.998x10^{-5}$, (2) $3.996x10^{-5}$,(3) $5.994x10^{-5}$, (4) $7.992x10^{-5}$ mol. dm^{-3}].

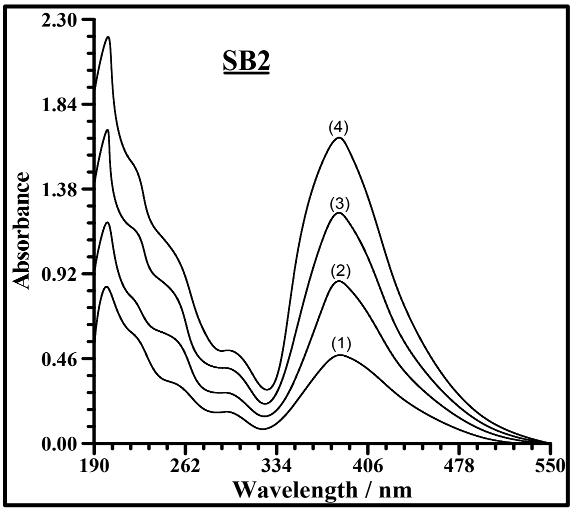


Figure (6): Electronic spectrum of SB2 in ethanol [(1) $1.584x10^{-5}$, (2) $3.168x10^{-5}$, (3) $4.752x10^{-5}$, (4) $6.336x10^{-5}$ mol. dm^{-3}].

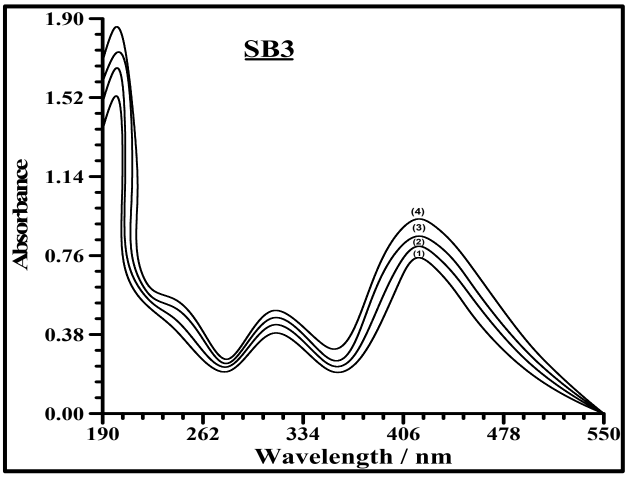


Figure (7): Electronic spectrum of SB3 in ethanol .[(1) 2.256×10^{-4}, (2) 3.384×10^{-4}, (3) 3.572×10^{-4}, (4) 3.760×10^{-4} mol. dm^{-3}].

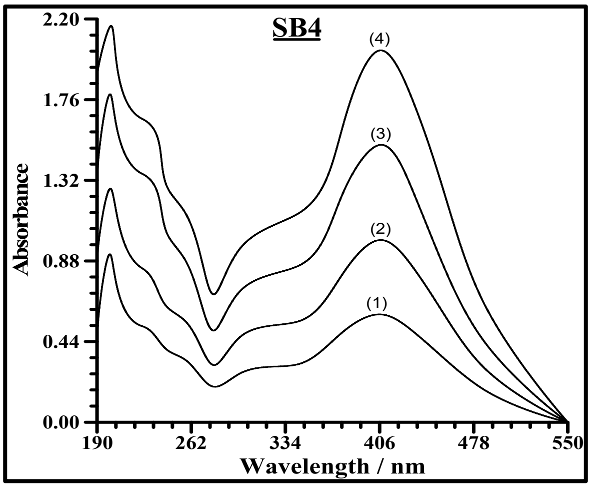


Figure (8): Electronic spectrum of SB4 d in ethanol [(1) 2.04×10^{-5}, (2) 4.08×10^{-5}, (3) 6.12×10^{-5}, (4) 8.16×10^{-5} mol. dm^{-3}].

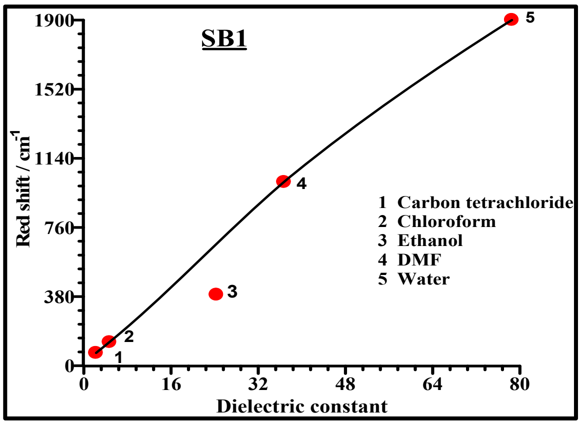


Figure (9): The relationship between dielectric constant and red shifts for SB1.

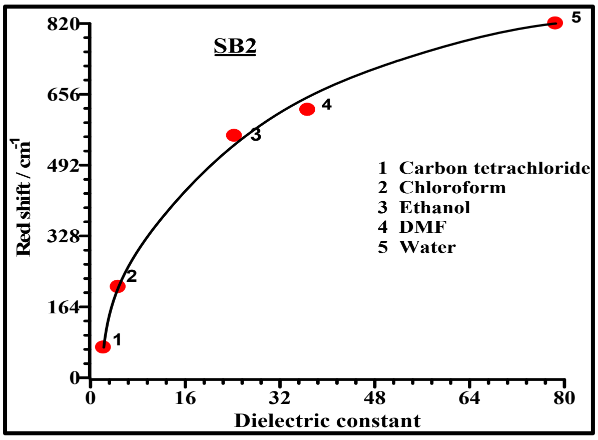


Figure (10): The relationship between dielectric constant and red shift for SB2.

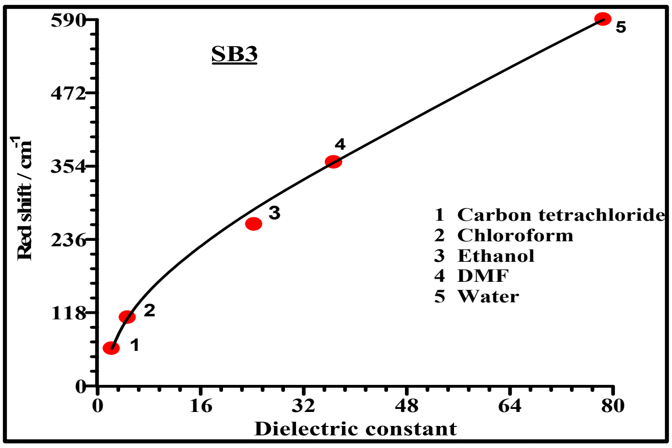


Figure (11): The relationship between dielectric constant and red shift for SB3.

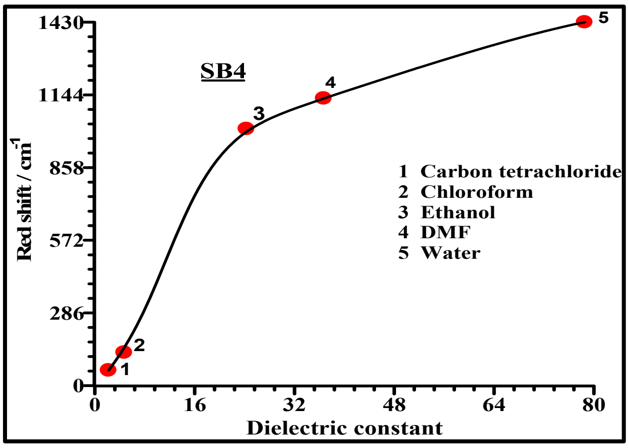
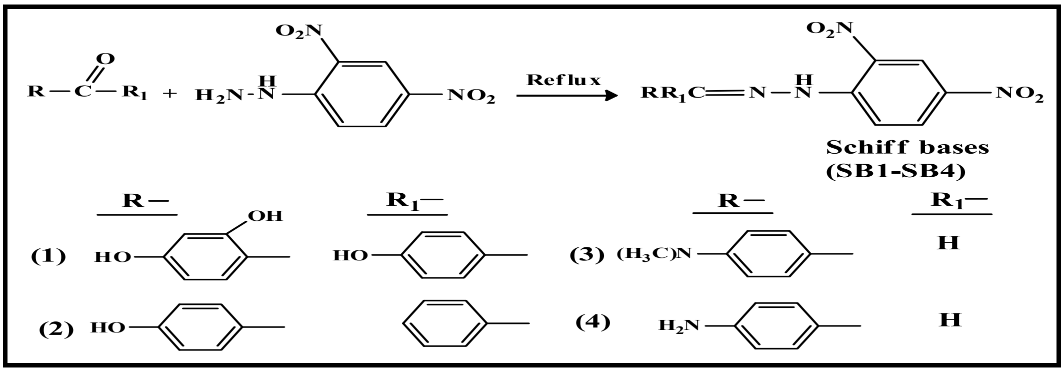
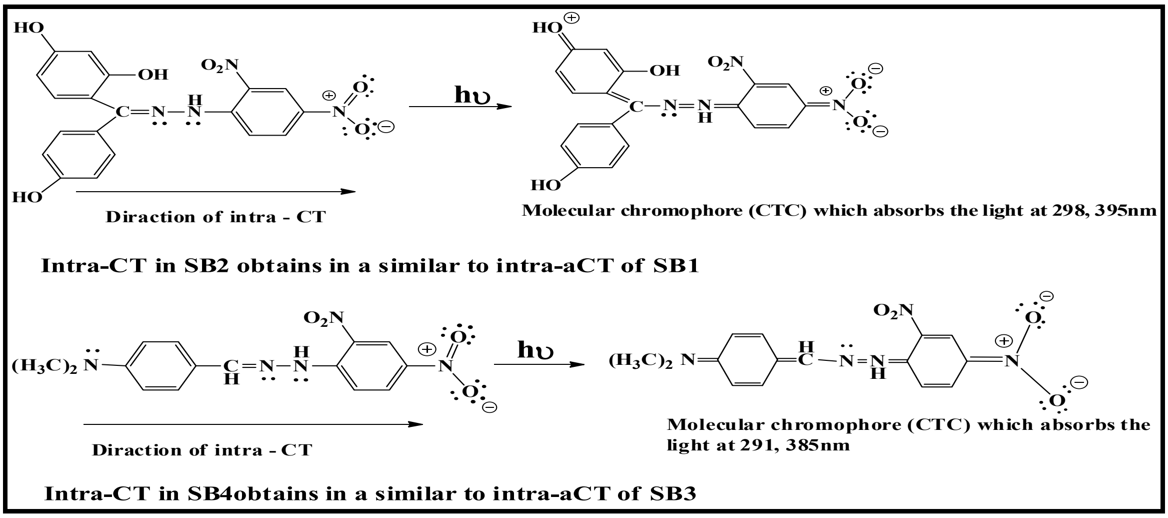


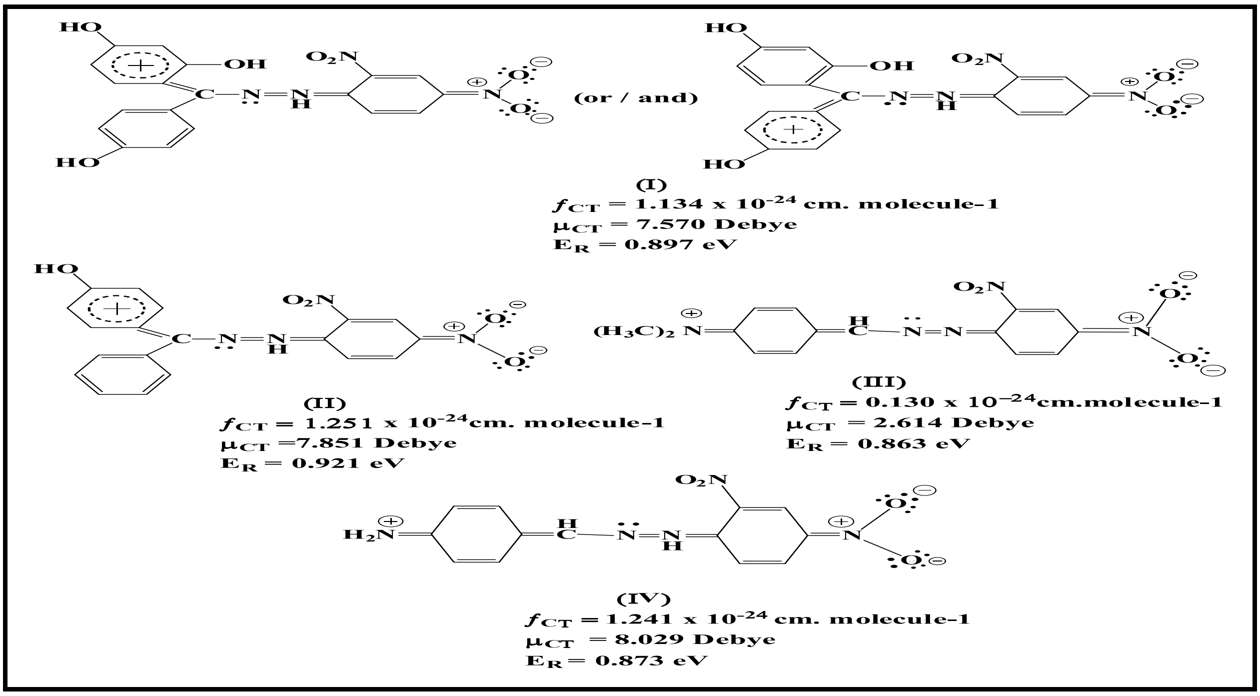
Figure (12): The relationship between dielectric constant and red shiftfor SB4.



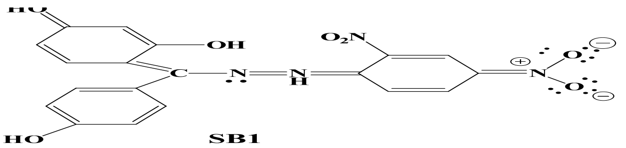
Scheme (1): Synthesis of new Schiff bases.



Scheme (2): Intramolecular charge-transfer in the synthesized aromatic Schiff bases.

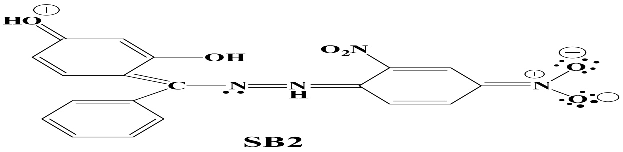


Scheme (3): Molecular structures of intramolecular CT complexes of SB1to SB4 which be responsible for light absorption and values of physical parameters.



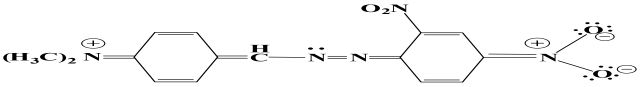
SB1

389	Cyclo C_6H_{12}
390	CCl_4
391	$CHCl_3$
395	C_2H_5OH
405	DMF
420	H_2O



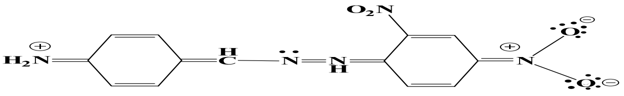
SB2

λ_{CT}/ nm	Solvent
377	Cyclo C_6H_{12}
378	CCl_4
380	$CHCl_3$
385	C_2H_5OH
386	DMF
389	H_2O



SB3

λ_{CT}/ nm	Solvent
407	Cyclo C_6H_{12}
408	CCl_4
409	$CHCl_3$
411	C_2H_5OH
413	DMF
417	H_2O



SB4

λ_{CT}/ nm	Solvent
390	Cyclo C_6H_{12}
391	CCl_4
392	$CHCl_3$
406	C_2H_5OH
408	DMF
413	H_2O

Scheme (4): Excited molecular shapes of intramolecular CT complexes and λ_{max}in different solvents.

تحضير وتشخيص طيفي لبعض قواعد شف الاروماتية الجديدة المشتقة من 4,2-ثنائي نيتروفنيل هيدرازين

أنور ذيب محمود الذيب
نور علي خضير
قسم الكيمياء / كليه العلوم / جامعة بغداد

استلم في:29/كانون الأول/ 2015،قبل في31:/كانون الثاني/2016

الخلاصه

حضرت اربع قواعد شف اروماتية جديدة لا تتحلل مائيا بالظروف الاعتيادية في هذه الدراسة بتفاعلاتالتكاثف بين 2- ,4ثنائي نيتروفينل هيدرازين:اولا مع2,4,4′- ثلاثي هيدروكسي بنزوفينون ليعطي SB1 وثانيامع 4-هيدروكسي بنزوفينون ليعطي SB2و, ثالثا مع 4- ثنائي مثيل امينوبنزالديهايد ليعطي SB3 ورابعا مع 4-امينوبنزالدهايد ليعطي SB4. لقد شُخصت التراكيب الجزيئية لقواعد شف الاروماتية هذه على اساس تعيين درجات انصهارها وتحليل العناصر الدقيق وتسجيل اطيافها تحت الحمراء وفوق البنفسجية-المرئية. ان الانتقالات الالكترونيه التي تم الحصول عليها درست في مذيبات الايثانول وثنائي مثيل فورمايد والماي والكلورفورم ورابع كلوريد الكاربون والهكسان الحلقي, وتعود حزم الامتصاص المسجلة في مذيب الايثانول الى انتقالتها الالكترونيه المناظره.تعود حزم الامتصاص التي تم الحصول عليها عند 291 الى 411 نانومترا في الاطياف الالكترونية لقواعد شف الاروماتية الجديدة المحضرة الى الانتقالات $(\pi \rightarrow \pi^*)$ الناشئة من حلقات البنزوفينون والالديهايد المعوضة والممتدة على طول الجزيئة في قواعد شف. عدَّت هذه الانتقالات بانها حزم معقدات انتقال- الشحنة الضمني إذ حيث تلعب اجزاء حلقات البنزوفينون والبنزالديهايد المعوضه كواهبات للشحنة وحلقه الفينيل هيدرازين المعوضه كمستقبل للشحنة. وايضا تم قياس ومناقشة تأثير المذيبات القطبية وغير القطبية في الانتقالات الالكترونية لحزمه معقد انتقال-الشحنة.

حسبت ونوقشت المعاملات الطيفية والفيزياوية للهيئات التركيبة الجزيئية لجزيئات معقدات انتقال-الشحنة الضمني مثل طاقات الانتقال ومعامل الامتصاص المولاري وشدة التذبذب الجزيئي وعزم ثنائي القطب الجزيئي الانتقالي وطاقه الرنين الجزيئي.

الكلمات المفتاحية: قواعد شف، معقدات شف، معقدات انتقال الشحنة، طيف الاشعة تحت الحمراء، الأشعة المرئية فوق البنفسجية، تحليل العناصر الدقيقة