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Spectroscopic study of some aromatic hydrazones derivated from aromatic substituted benzophenones and benzaldydes

Anwar T.M.AL-Thib, Noor A.Khudhair*
Department of Chemistry, Collage of Science, Baghdad University, Baghdad (IRAQ)
E-mail : mohanndk@yahoo.com

ABSTRACT

Four novel aromatic hydrazones not hydrolysed under ordinary conditions were synthesized in this research by condensation reactions between 2,4-dinitrophenylhydrazine: firstly with 2,4,4‘-trihydroxybenzophenone to give I, secondly with p-hydroxybenzophenone to give II, thirdly with p-dimethylaminobenzaldhyde to give III and fourthly with p-aminobenzaldehyde to give IV. The molecular structures of these aromatic hydrazones obtained were characterized based on melting points, elemental analysis and UV-Visible spectra. The electronic absorption spectra of hydrazones obtained were studied in different solvents of ethanol, DMF ($(CH_3)_2NCHO$), water, chloroform, carbon tetrachloride and cyclohexane. The appeared absorption bands in ethanol solvent were attributed to corresponding electronic transitions, and discussed. The absorption bands at 291 to 411 nm obtained in electronic spectra of the synthesized new aromatic hydrazones were attributed to $(\pi\rightarrow\pi^*)$ transition which arise from substituted aromatic benzophenone or benzaldehyde rings and directed along of molecule in hydrazones. These transitions are supposed to represent the intramolecular charge-transfer (CT) complexes bands in which the substituted two halves of benzophenone and benzaldehyde rings are as charge donors and the substituted phenylhydrazine ring is the charge acceptor. Also, the effect of non-polar and polar solvents on the electronic spectra have measured and discussed. The physical-spectroscopic coefficients in molecular structural shapes of intra CT complexes molecules such as transition energies (E_{CT}), molar extinction coefficients (ε_{CT}), molecular oscillator strength (f_{CT}), transition molecular dipole moment (μ_{CT}) and molecular resonance energy (E_R) have been calculated and discussed.

KEYWORDS

Hydrazones;
Charge-transfer complexes;
Polar and non-polar organic solvents.

INTRODUCTION

Hydrazones are an important species of organic Schiff bases compounds, where prepared in 1864 by a German chemist, Hugo Schiff, Nobel Prize winner[1]. These compounds are prepared from condensation of hydrazine compounds with carbonyl compounds such as benzophenones, acetophenones or benzaldehydes. Structurally, hydrazone compound which also known as hydrazone class is an analogue of aldehyde or ketone of aldehyde or ketone in which the carbonyl group will be replaced by an hydrazone group (CH=N-NH, C=N-NH-)[2,3]. The preparation of hydrazones is reversible reactions and takes place under acid catalysis or by direct fusion[4-6]. In recent years, hydrazones 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 hydrazone group in hydrazones have been shown to be decisive to their biological activities[12,13]. Hydrazones are a set of organic intermediates which are used also in the synthesis and chemical analysis. They are used in the production of the medications and agrochemical industry. The transition elements and the other certain metallo-elements are known to form aromatic hydrazones complexes[14,15]. Aromatic hydrazones behave as flexidentate ligands and ordinarily coordinate through nitrogen atom of hydrazone group, oxygen atom of the de-pronated phenolic group and other donor atoms[16]. Charge-transfer complexes of hydrazones are great importance in chemical interaction, including intramolecular charge-transfer complexes, biochemical and bioelectrochemical energy transfer processes, biological systems, drugs- acceptors binding mechanisms and medications analysis[17-20]. Moreover, charge-transfer complexations are of great importance in many applications and fields, such as conductivities of materials, optical activities, surface chemistry, solar energy storage, semiconductors and investigations of redox processes[21-23]. Based on this, we decided preparation novel aromatic hydrazones are not hydrolysed under ordinary condition, and derived of 2,4,4‘-trihydroxybenzophenone, 4-hydroxybenzophenone, 4-dimethylaminobenz aldehyde and 4-aminobenzaldehyde with 2,4-dinitrophenylhydrazine may fit-those purpose, then characterization of molecular structures by elemental analysis (CHN) and UV-Visible. The study is also including explanation of electronic transitions, determination of the physical spectroscopic coefficients and their discussion.

EXPERIMENTAL

Chemical materials

The chemicals used in this research 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 (DMF) were of Spectroscopic grade were supplied by BDH Company. Organic compounds of p-hydroxybenzophenone (98% purity grade) and 2,4-dinitrophenylhydrazine (99% purity grade) were supplied by Merck Company, p-Aminobenzaldehyde and p-dimethylaminobenzaldhyde (99% purity grade) were supplied by BDH Company, while 2,4,4‘-trihydroxybenzophenone (98% purity grade) was supplied by INC Company.

Instruments

Melting points were recorded using Gallenkamp melting points apparatus from Varian Company which measures the extent to 280°C. The elemental analyses (carbon, hydrogen and nitrogen elements) were determined using a Perkin-Elmer CHN 2400 (USA). The electronic absorption spectra were recorded in different solvents over wavelength range of 190-900nm by the Varian DMS 100 UV-Visible double-beam spectrophotometer.

Synthesis of hydrazones

Four new aromatic hydrazones were prepared as follows: (1) hydrazone I was prepared by mixing equimolar amounts of 2,4-dinitrophenylhydrazine (m.p. 197-200 °C) and 2,4,4‘-trihydroxybenzophenone (m.p. 196-197°C), both dissolved in 25 ml ethanol solvent then added two drops of concentrated HCl. The reaction mixture was heat under back reflux for 7 hour, after cooling maroon crystals product was separated, then filtered. The solid product was recrystallized by ethanol, then dried. Melting point of I was recorded higher than 280°C. Hydrazone II prepared by mixing equimolar amounts of 2,4-dinitrophenylhydrazine and p-hydroxybenzophenone (m.p. 110-112°C), both dissolved in 25 ml ethanol solvent and added two drops of concentrated HCl. The reaction mixture heated under back reflux for 1.5 hour, after cooling orange precipitate was separated, then filtered. The solid precipitate was recrystallized by ethanol, and then dried. Melting point of II was recorded 218-220°C. Hydrazone III prepared by mixing equimolar amounts of 2,4-dinitrophenylhydrazine and p-dimethylaminobenzaldhyde (m.p. 73-75°C), both dissolved in 30 ml methanol solvent and then added 3 drops nearly of concentrated HCl. The reaction mixture heated under back reflux for 1.5 hour, after cooling black precipitate was separated in solution, and then filtered. The black precipitate was crystallized by methanol, then dried. Melting point of III was recorded than 235-237°C. Hydrazone IV was prepared by mixing equimolar amounts of 2,4-dinitrophenylhydrazine and p-aminobenzaldehyde (m.p. 165-168°C), both dissolved in 30 ml methanol solvent and added two drops of concentrated HCl. The reaction mixture heated under back reflux for 1.5 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 IV was recorded higher than 184-186°C. The molecular structures of these hydrazones characterized and identified by their melting points, elemental analysis (CHN) and UV-Visible.

Preparation of samples solutions

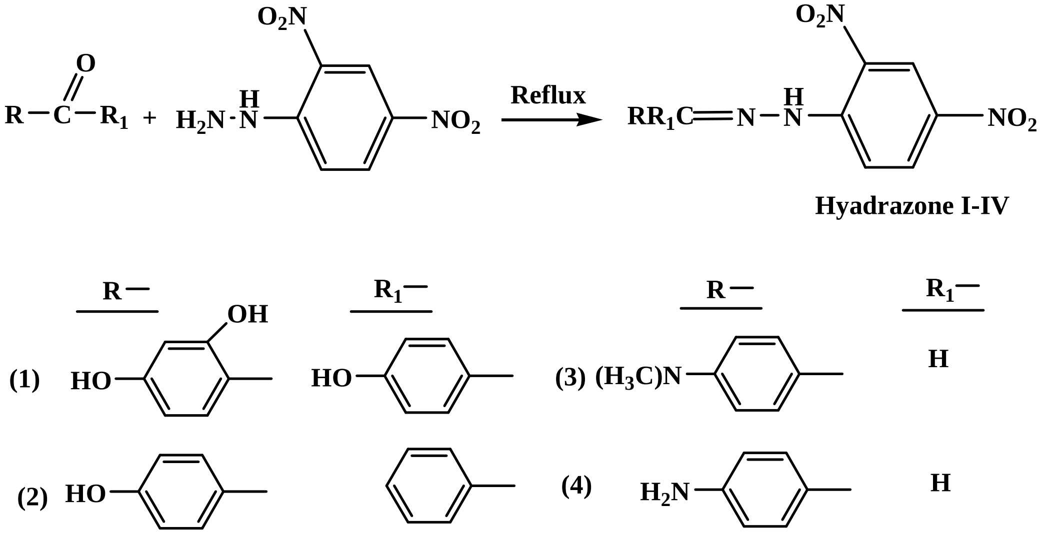
Standard solutions were prepared for spectral measurements of the materials that included in this research from 2,4-dinitrophenylhydrazine, aromatic carbonyls derivatives and the prepared new aromatic hydrazones in gravimetric method. We weight the required amounts from solute substance in certain volume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

RESULTS AND DISCUSSION

Chemistry and characterization

Novel four hydrazones have been synthesized from the condensation 2,4-dinitrophenyl hydrazine with 2,4,4‘-trihydroxybenzophenone, p–hydroxybenzophenone, p-dimethylamino benzaldehyde and p-aminobenzaldehyde (Scheme 1). They are stable at room temperature and commonly soluble in methanol, ethanol, water and dimethylformamide. The elemental analysis, yield percentage physical state, color and melting point of these hydrazones I-IV are presented in TABLE 1.

From melting points in TABLE 1, it is expected that there in hydrazone I 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 hydrazone I, II and III, > 280, 218 and 235°C respectively, are higher than hydrazone IV. However, melting point of hydrazone IV is lower

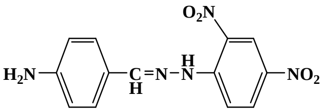


Scheme 1 : Synthesis of new hydrazones

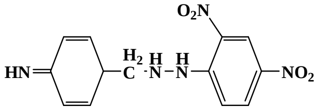
TABLE 1 : Physical characterization and elemental analysis CHN data of new hydrazones I – IV

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

(184°C) than hydrazone I which include intra- and intermolecular hydrogen bonding. Some substituted aromatic hydrazones exhibit the ketamine tautomeric shapes and their common feature is presence of the substituted hydroxyl or amino group on the aromatic ring[24]. The low melting point of hydrazone IV may be explained by (I) and (II) tautomerism shapes as shown below:



(I)



(II)

Electronic spectra and their explanation

Figure (1) to (4) represent the electronic spectra of the synthesized new aromatic hydrazones which contain on substituted phenyl rings with hydroxyl, dimethylamino, amino or nitro and azomethine groups. TABLE (2) 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 I to IV 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 are absorption intensities of these bands decreases for their values compared with the intensity value at 184nm (6000 $m^2.mol^{-1}$) of benzene ring[25,26]. This can be explained due to azomethine and nitro groups presence which do as electron-withdrawing groups and cause an inductive

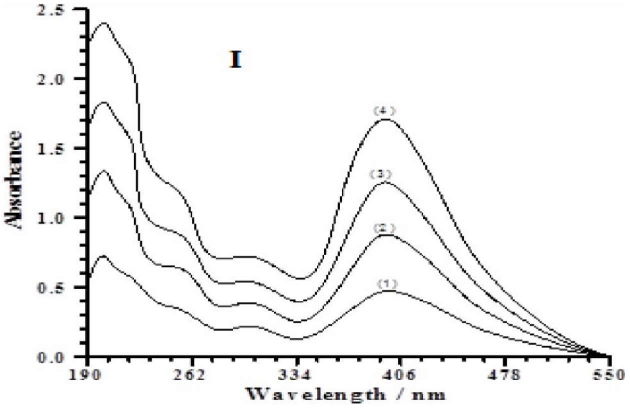


Figure 1 : Electronic spectrum of I in ethanol (1) 1.998 * 10^{-5}, (2) 3.996 * 10^{-5},(3) 5.994 * 10^{-5}, (4) 7.992 * 10^{-5} mol. dm^{-3}]

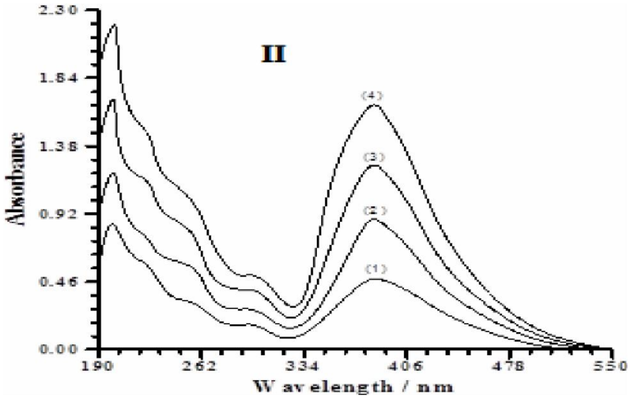


Figure 2

effect in each of I to IV, hence decreases the transition intensities on the aromatic substituted phenyl rings[6,25].

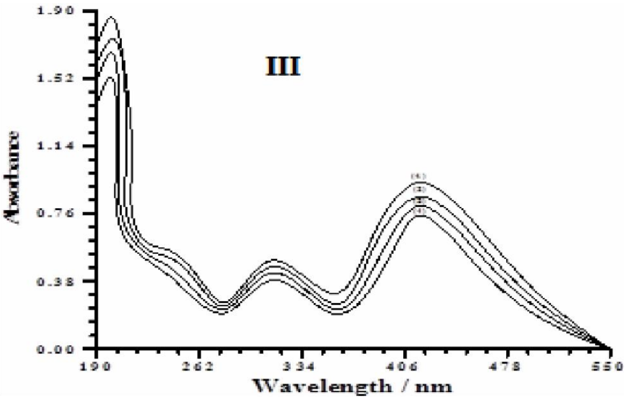


Figure 3 : Electronic spectrum of III in ethanol. [(1) 2.256 * 10^{-4}, (2) 3.384 * 10^{-4}, (3) 3.572 * 10^{-4}, (4) 3.760 * 10^{-4} mol. dm^{-3}]

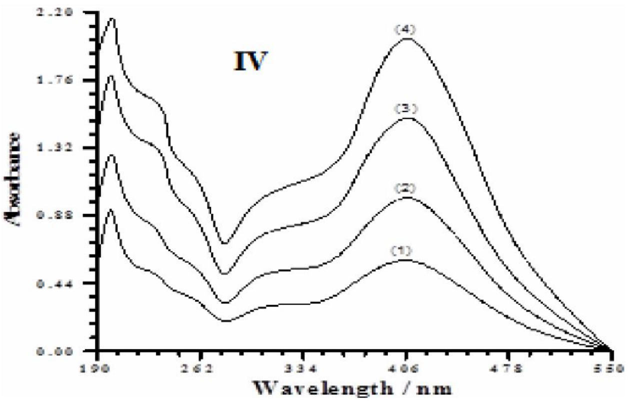
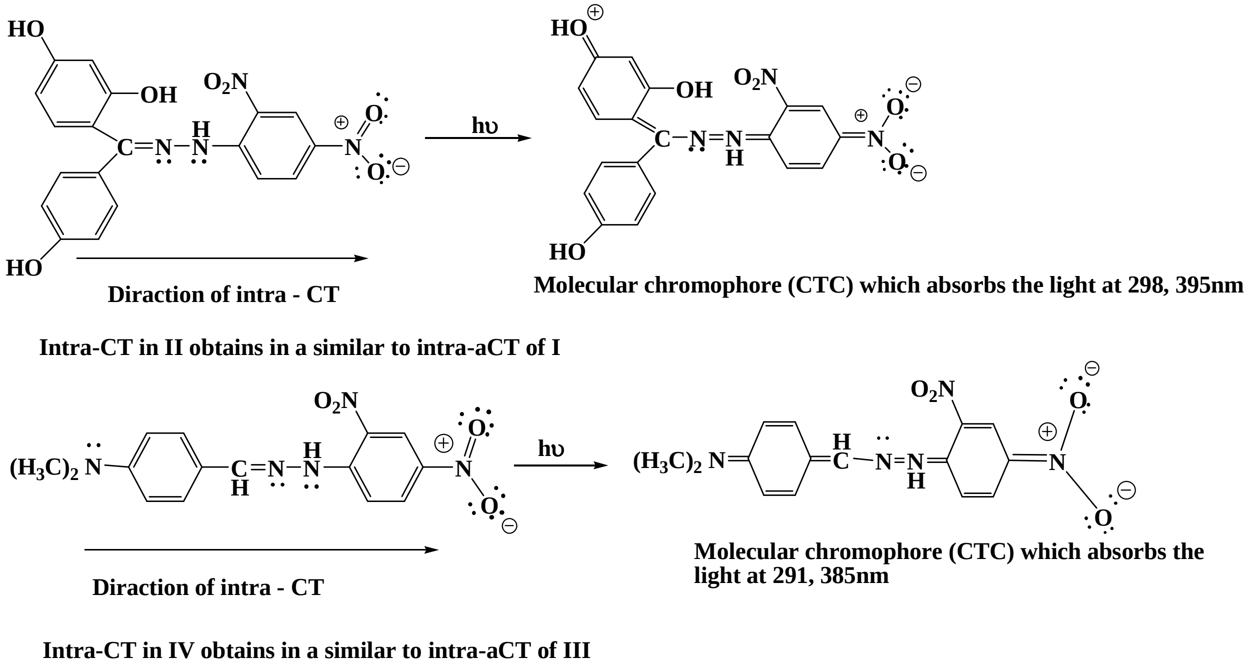


Figure 4

The absorption bands 207, 217 and 222 nm all shoulders in electronic spectra of I, II and IV respectively represent the local excitations (π→π*) transitions of substituted phenyl rings which correspond the electronic transition ($^1A_{1g} \rightarrow {}^1B_{1u}$) at 203nm of benzene ring[25]. We think that the absorption bands for this transition in III 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 I to IV respectively, represent the local excitations (π → π*) 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 I to IV respectively, all these bands represent (π→ π*) transitions which are originated from substituted groups as electron-donating groups on carbonylic ring, and extended over the whole hydrazones molecule to substituted 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 hydrazone molecule enhances such transition[25,27]. Theses absorption bands can suggest there due to intramolecular charge transfer effect of the formed molecular



Diraction of intra - CT

Molecular chromophore (CTC) which absorbs the light at 298, 395nm

Intra-CT in II obtains in a similar to intra-aCT of I

Diraction of intra - CT

Molecular chromophore (CTC) which absorbs the light at 291, 385nm

Intra-CT in IV obtains in a similar to intra-aCT of III

Scheme 2 : Intramolecular charge-transfer in the synthesized aromatic hydrazones

TABLE 2 : Electronic spectra bands data of the prepared aromatic hydrazones in ethanol solvent attemperature 20°C

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

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

chromophore which includes electron donor part and electron acceptor part within the same molecule of hydrazone. These intracharge-transfer states are similarly to the intracharge-transfer in p-nitroaniline molecule which absorbs the light at 376nm as follows[27-30]. Scheme 2 represents molecular chromophores of intramolecular charge-transfer complexes in the synthesized new aromatic after light absorption of hydrazones.

Spectroscopic-physical coefficients of infra CT complexes

The spectroscopic and physical coefficients of intracharge-transfer complexes in I to IV, such as transition energy (E_{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 I to IV dissolved in ethanol solvent at 20°C. All values have been appointed by charge-transfer band with least energy in the electronic spectra of I-IV as shown in the Figures (1) to (4). 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).

$$E_{CT}(eV) = 1240.8\ (nm.\ eV) / \lambda_{max}(nm) \qquad (1)$$

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

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

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)

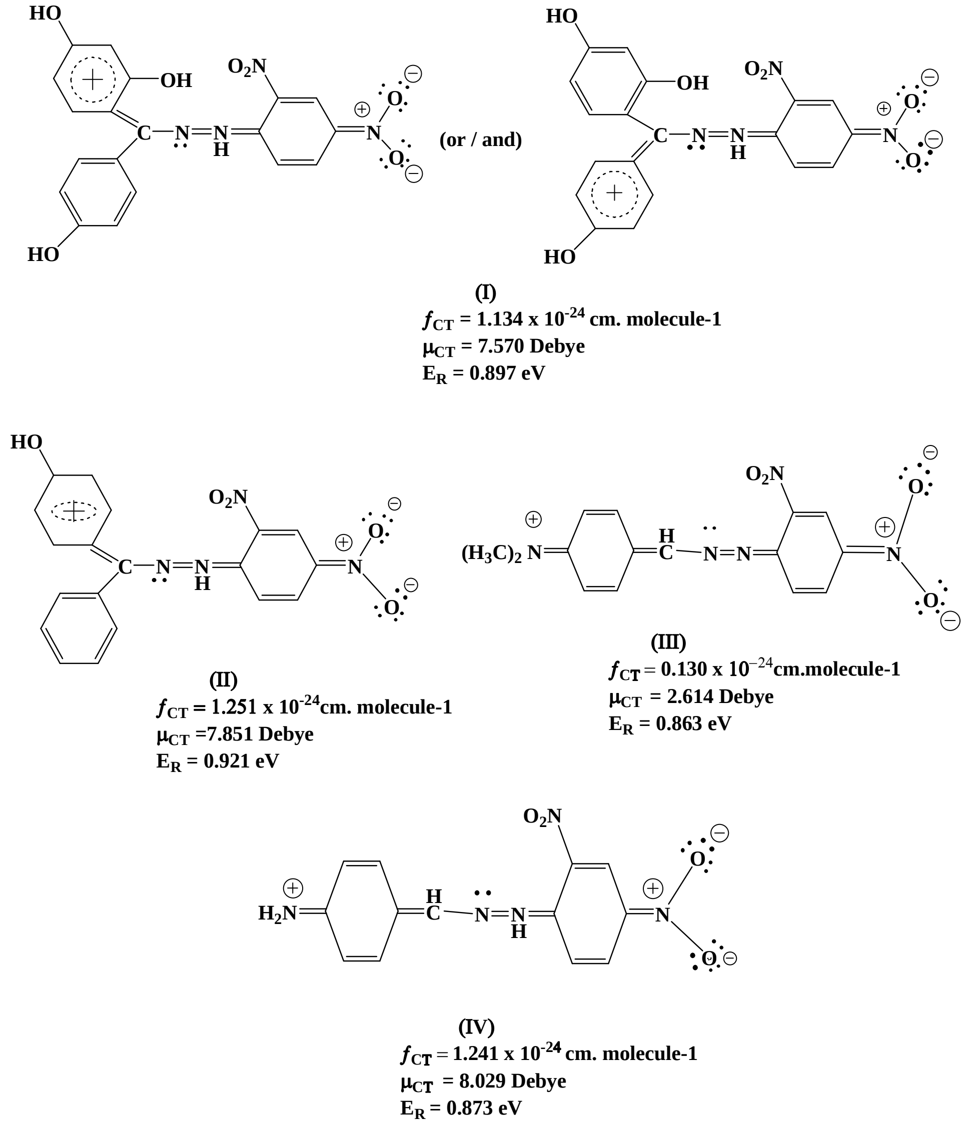
$$\mu_{CT} = 9.582 * 10^{-2} \left(\frac{\varepsilon_{CT} . \Delta\bar{\upsilon}_{1/2}}{\bar{\upsilon}_{1/2}} \right)^{1/2} \qquad (3)$$

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 determines how the molecular system will interact with an electromagnetic wave, while the square of the value

TABLE 3 : The values of transition energy, oscillate strength and values of transition dipole moment of intramolecular CT complexes for the synthesized aromatic hydrazones I-IV in ethanol solvent and temperature 20°C

Hydra--zones	λ_{max}/nm	$h\upsilon_{CT}$/ eV	ε_{CT} / $dm^3.mol^{-1}. cm^{-1}$	$\Delta\bar{\upsilon}_{1/2}$/ cm^{-1}	f_{CT}/ $cm.molecule^{-1}*10^{22}$	μ_{CT}/ Debye	E_R/ eV
I	395	3.141	21923	7207	1.134	7.570	0.897
II	385	3.223	28323	6156	1.251	7.851	0.921
III	411	3.019	2223	8143	0.130	2.614	0.863
IV	406	3.056	24852	6956	1.241	8.029	0.873

(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



(I)
f_{CT} = 1.134 x 10^{-24} cm. molecule-1
μ_{CT} = 7.570 Debye
E_R = 0.897 eV

(II)
f_{CT} = 1.251 x 10^{-24}cm. molecule-1
μ_{CT} =7.851 Debye
E_R = 0.921 eV

(III)
f_{CT} = 0.130 x 10^{-24}cm.molecule-1
μ_{CT} = 2.614 Debye
E_R = 0.863 eV

(IV)
f_{CT} = 1.241 x 10^{-24} cm. molecule-1
μ_{CT} = 8.029 Debye
E_R = 0.873 eV

Scheme 3 : Molecular structures of intramolecular CT complexes of hydrazones I to IV which responsible for light absorption and values of physical parameters

TABLE 4 : Variation of red shift ($\Delta\bar{\upsilon}$/cm^{-1}) with dielectric constant of the solvent (ε*) for highest wavelength absorption band in different solvent at temperature 20°C(λ_{CT}/nm, $\bar{\upsilon}_{CT}$/cm^{-1})

Solvent	$^{*}\varepsilon$	I			II			III			IV		
		λ_{CT}	$_{CT}\bar{\upsilon}$	Δ $_{CT}\bar{\upsilon}$	λ_{CT}	$\bar{\upsilon}_{CT}$	$\bar{\upsilon}\Delta_{CT}$	λ_{CT}	$\bar{\upsilon}_{CT}$	$\bar{\upsilon}\Delta_{CT}$	λ_{CT}	$\bar{\upsilon}_{CT}$	$\bar{\upsilon}\Delta_{CT}$
Cyclo-C_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

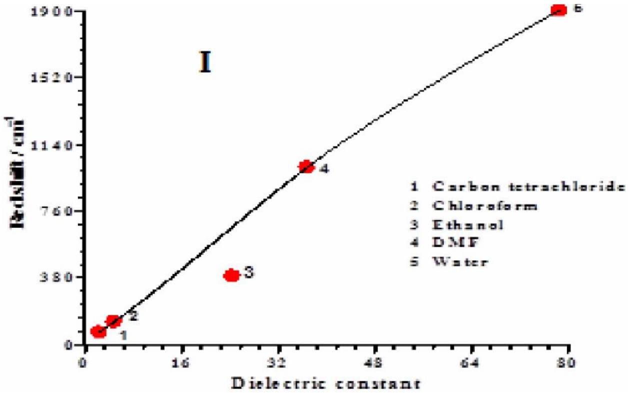


Figure 5 : The relationship between dielectric constant and red shifts for I

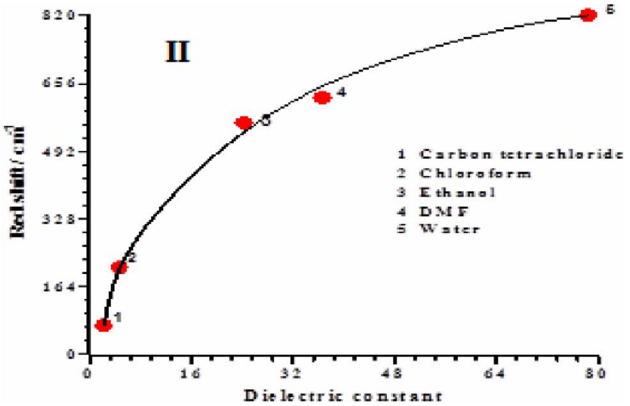


Figure 6 : The relationship between dielectric constant and red shift for II

complex molecule in has been estimated by the theoretical equation (4)[33].

$$E_R = \frac{E_{CT} \cdot \varepsilon_{CT}}{7.7{*}10^{-4} + (3.5\,\varepsilon_{CT})} \tag{4}$$

Where value (7.7*10^{-4}) is the same unit of ε_{CT} (dm^3.mol^{-1}.cm^{-1}), 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 value reflects obviously as contributing factor to stability of the molecular chromophores of intramolecular charge-transfer complex molecule[28].

Returning to TABLE 3, 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 hydrazones molecules from I to II, as well as from III to IV except molecular resonance energy (E_R) value of III is less. The stability of hydrazone III is less compared with hydrazone IV due to the steric hindrance effect of dimethyl groups with unshared-pair of electrons on nitrogen atom[25]. The results of the

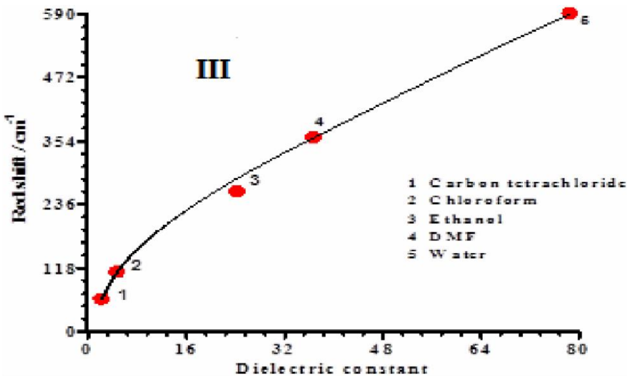


Figure 7 : The relationship between dielectric constant and red shift for III

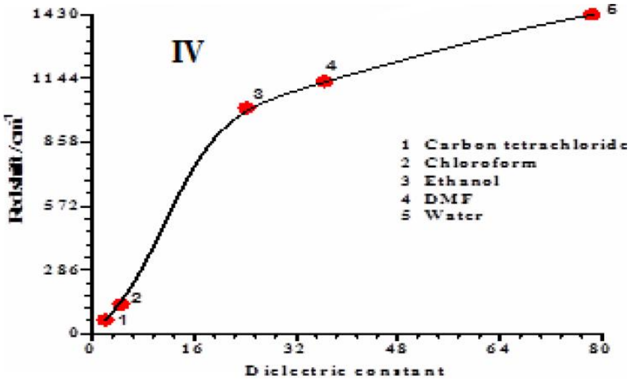


Figure 8 : The relationship between dielectric constant and red shift for IV

($h\upsilon_{CT}$) 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 hydrazones I, II and IV 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 I to IV which can be responsible for light absorption, and the values of physical parameters (f_{CT}, μ_{CT}, E_R).

Effect of solvent polarity on the electronic transitions

Clearly, the data seem that the polar and nonpolar solvents have not effect on the absorption band at 193-263nm in the electronic spectra of I to IV, but there is marked effect on the longer wavelength absorption bands than 285 nm. TABLE (4) shows such effects and Figures (5) to (8) illustrate that the red shift ($\Delta\bar{\upsilon}$) in λ_{max} for longest wavelength absorption band of I-IV. The red shift increase rapidly with increasing dielectric constant of the solvent until the value (50) nearly for I, (30) for II, (10) for III, and (24.33) for IV, 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 hydrazone molecule becomes more polar than its ground state, therefore the polar solvent stabilizes the excited state by connection dipole of hydrazone molecule with positive and negative ends of the solvent molecules. The more delocalization of the charge in the excited state of hydrazone molecule, higher increase of red shift ($\Delta\bar{\upsilon}$) with dielectric constant occurs. This effect is very clear in all cases of I-IV. In these molecules there are hydroxyl, amino and dimethylamino groups which increase the delocalization of the charge in hydrazone molecule and leading to higher values of red Shift.

CONCLUSION

We observed from research data in this study, existence of intra CT complexes within the molecular shapes of these hydrazones. 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 hydrazones molecules.

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