Synthesis and Study the Characterization of (4,5-dihydroxy-3-((4- aminodiphenylsulfone) phenyl)diazenyl)naphthalene-2,7-disulfonic acid effect pH on the a New Azo Dye Compound and study of the Structure, Electronic Properties and Intramolecular Hydrogen Bonding (IHB)

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Abstract: New azo dye was prepared from 4,4-diaminodiphenyl sulfone with chromotrpic acid. The prepared by fox method, dye azo were identified by IR-spectrophotometry, visible spectroscopy and (CHN) analysis. The absorption spectra of the azo dye was recorded with wavelength in the range (360-650)nm in universal buffer solution of different pH values. From these spectra, the ionaization and protonation constant were calculated by using the half height method. It found that the value of the ionaization constant(pKa) closely which interpret the ionaization of the hydroxyl group. Theoretical calculations for azo dye with and without intramolecular hydrogen bonding(IHB) were studied by quantum chemical calculations for the first time. The optimized structures of the azo dye were obtained by molecular mechanics (MM+),

and then further geometry optimization was carried out by the semi-empirical molecular orbital theory at the level of AM1 of the theory. Study Shown, the configuration II more stable with (IHB). Also the dipole moment, heats of formation, molecular orbitals energy of HOMO and LUMO and energy band gaps (ΔE) were calaulated

KeyWord: Azo dye Compound Derivative from chromotropic acid, Analytical Study, Electronic Properties

Introduction

Azo dyes are characterized by a chromophoric azo group –N=N-, whose nitrogen atoms are linked respectively to SP^2-hybridized carbon atoms (1). At least one of these carbon atoms belongs to an aromatic carbocycle (usually a benzene or naphthalene derivative) or heterocycle, whereas the second carbon atom adjoining the azo group may also be part of an enolizable aliphatic derivative (2). The most common types of azo dyes can be summarized as follows: aryl –N=N-R, where R can be an aryl, heteroaryl, or –CH=C (OH)-alkyl due to the simple nature of the synthesis, usually in aqueous medium and the almost unlimited choice of starting products, an extremely wide variety of azo dyes is possible.

The synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophilic aromatic compound such as an aryl amine or a phenol (3-4).

Azo dyes can be classified either according to chemical guideline (characteristic chemical groups) or by color aspects (application in dye works) (5). Many investigations (6-10) showed that such compounds are of great

pharmaceutical importance as they have a diabetogenic and bacteriostatic properties. In industry. Azo dyes are the most important class of industrial dyes. An acid-base indicator is an organic compound that changes color with a change in pH. Methyl orange is a very common acid-base indicator, red in solutions that have pH values less than 3.2 and yellow in solutions with pH greater than 4.4. Indicators change color because the chromophoric system is changed by an acid base reaction(11-12). The basicity and acidity constants of the different azo compounds were determined from the spectra in aqueous-ethanol solutions of varying pH values(13).

In the present study a new azo compound was prepared which in (4,5-dihydroxy-3-((4- aminodiphenylsulfone) phenyl)diazenyl)naphthalene-2,7-disulfonic acid) and identification include by IR, and Visible spectroscopy, elemental analysis (CHN) and study of azo dye acide-base properties and its application as an indicator for acid-base titration as well study of the structure, electronic properties and intramolecular hydrogen bonding (IHB) properties were studied .

Experimental

Chemical Material

Methanol, Ethanol, chromotropic acid disodium salt dehydrate, sodium hydroxide from (Fluka Co.), 4,4-diaminodiphenyl sulfone, sodium nitrite, hydrochloric acid from (Merck Co), were purified before using (14). IR spectra were recorded on a Buck Scientific Model 500. IR spectrophotometer using a KBr disc in the range (4000 – 500) cm^{-1}. Absorption Spectra in Methanol were determined

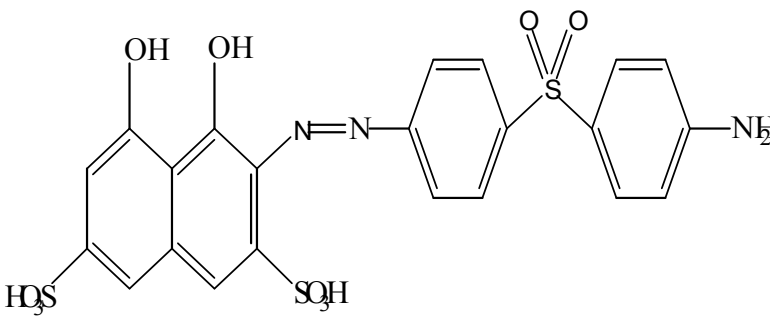
on a U-1500- HITACH UV–Visible spectrophometer. The melting Point of the compound were determined with a 9300 Model – Electro thermal melting point. The pH values of buffer solutions were measured using pH meter model DIGI 520 made by WTW Company. FT-IR, UV-Visible spectrophotometer and melting point was performed by Chemistry Department – Education College – Basrah University. Elemental analysis (CHN) of the compounds were determined with Euro Vector EA 3000A Italy was performed by al-bayt university.

Methods

A-Synthesis of the Azo Dyes

The above azo dyes were prepared by a method similar to that described by Fox [15]. In the present method the dyes were prepared as following:

The resulting azo dye, 94% yield , m.p. >346 ^{0}C . Azo dye have been characterized by elemental analysis and IR , UV spectra. The structure of the azo dye in Scheme (1).



Scheme1. chemical structure of the *(*4,5-dihydroxy-3-((4-aminodiphenylsulfone) phenyl)diazenyl)naphthalene-2,7-disulfonic acid

B- Analytical Study

1- Preparation of Buffer Solutions of acetate

A series of buffer solutions covering the range of pH values (0.65 to 5.2) was prepared by mixing (25ml) (1M) sodium acetate with (47.5ml, 37.5ml, 30.0ml) hydrochloride acid(1M) to give pH (0.7, 1.0, 1.5)respectively. The pH values of the buffer solutions were checked by aid of a pH-meter[16-17].

2- Universal Buffer Solutions:

A series of buffer solutions covering the range of pH values(2 to 12) was prepared as recommended by Britton and Rhobinson [18] with modification involving titration of 50ml of the mixture (0.04M with respect to boric, acetic and phosphoric acids) with 0.2M sodium hydroxide to the desired pH and then making with water up to 250ml so as to keep the ionic strength almost constant at all pH values. The pH values of the buffer solutions were checked by aid of a pH-meter[17].

3- Solutions of Dyes:

The 0.001M dye solution was prepared by dissolving the (0.0290 gm) of the dye in the mixture of proper volumes of water+ ethanol (1:4, v/v) to the desired (50ml) Solutions of Dyes.

4- Spectrophotometric Methods for the Determination of pK Values of Azo Dyes:

The absorption spectra of the azo-dyes under investigation were scanned within the wavelength range (360-650)nm in universal buffer solutions covering the range of pH-values (0.7-12) for this purpose a known volume (0.5ml) of the aqueous solution of the azo compounds (10^{-3}M) was added in 5ml volumetric flask and

then made up to the mark with buffer solution. The spectra were obtained at room temperature figure 1. The study carried out in this part considered mainly two points:

a. The effect of pH on absorption spectra on the the azo dyes.

b. Determination of the ionization constant (pK_a) of the hydroxyl group and the protonation constant (pK_p) of the nitrogen atom. Half height method [19] was used for the determination of pK values. This method depends on the fact that the limiting absorption (A_l) represents complete conversion of one from of the compound to the other. Since pK is equal to pH at which the two forms exist in equivalent amount, then the pH corresponding to half the height of the absorbance. pH curve is equal to pK.

The pK value is given by relation:

$$\mathbf{pK = pH\ (at\ A_{1/2})} \ldots\ldots\ \mathbf{(1)}$$

Where:

$$\mathbf{A_{1/2} = \frac{A_l - A_{min}}{2} + \ldots\ldots\ (2)}$$

C- Computational Methods

Theoretical calculations were performed on hyperchem program version 7.5, running on a Pentium V PC-CPU 3400GHz. The geometries of the four compounds were optaimized first at level (MM+) by molecular mechanics

force field theory and then at level (AM1) by semi-empirical theory[20].

Result and Discussion

In this paper, The synthesis of azo dye from 4,4-diaminodiphenyl sulfone with chromotropic acid, were formed in good yield, and it is stable at room temperature and is nonhygroscopic. The elemental analysis for C, H and N is calculated . The results obtained are shown in Table (1). A reasonable agreement between the found and calculated data was found.

IR Spectra

The azo dye was identified by FT- IR spectroscopy in the range (4000–500)cm^{-1} as KBr discs (Figure 1). The stretching vibration of the OH groups which appeared in the region of (3458.45) cm^{-1}which is cancel the absorption peak of (-NH2) group supposed appear at same of the region . The band shows broad appearance due to its relatively low frequency. It can be concluded that the (-OH) groups may form a hydrogen bond with nitrogen atom. The band corresponding to (-N=N-) stretching vibration usually lies around (1434.94) cm^{-1} [21], the (-C=C-) stretching vibration of the aromatic ring shows of (1501.27) cm^{-1} . Stretching vibration of the (-C-H) aromatic appear at (3095.55) cm^{-1}. [21-22] The all mentioned bands were shown in table1.

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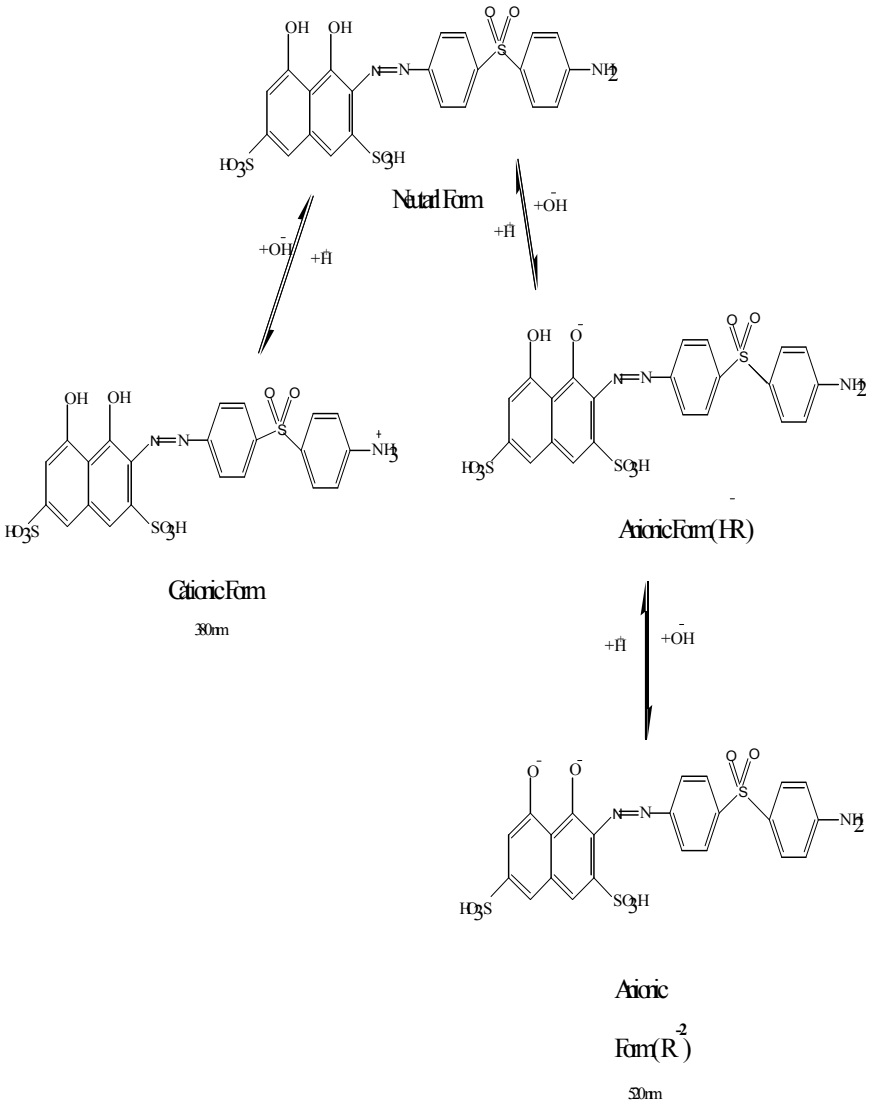
Table 1: IR, C.H.N data for azo dye compound

Wave numbers (cm^{-1})				Calculated (Found)(%)		
υ O-H & υ N-H br	υ C=C m	υ N=N s	υ C-H m	C	H	N
3458.45	1501.27	1434.94	3095.55	45.54 (45.23)	2.95 (2.66)	7.24 (6.94)

br:broad, s:sharp, m:medium

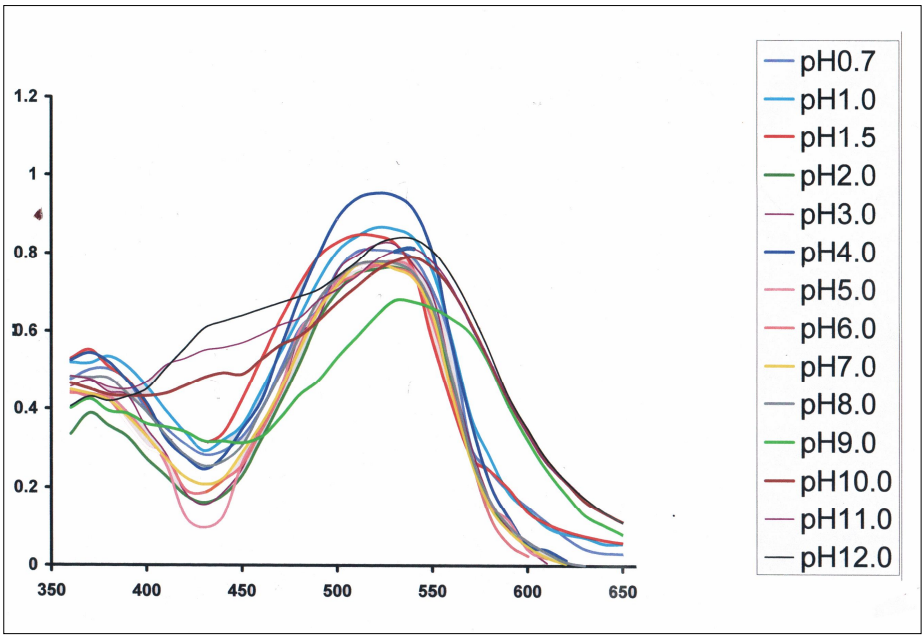
Absorption Spectra of Azo Dye in Buffer Solutions:

The absorption spectra of $8*10^{-5}$M solutions of azo dye in buffer solutions of varying pH values(0.7-12) are represented graphically in Scheme (2). The spectra of dye is characterized by two absorption bands absorbing maximally at 380 and 520nm. The shorter wavelength band appearing at low pH values (pH<4), this band is due to the absorption of the protonated form whereas the longer wave length band observed at higher pH (>7), due to the ionized species. On increasing the pH of medium, the absorbance of the shorter wavelength band decreases while that of the longer wavelength band increases due to the complete transformation of the dye molecule to the corresponding anion liable to predominate in alkaline solution as a result of the ionization of hydroxyl groups. The recorded spectra of dye possess three isobestic points at (400,480 and 560)nm within the pH range (0.7-12). These results indicate the existence of the following equilibria.



Scheme 2. Suggested mechanism equilibria of the azo dye compound

Figure 1. Absorption Spectra of $8*10^{-5}$M solution of azo dye at varying pH values



Determination of Ionization and Protonation Constants:

The ionization and protonation constants of studied azo dye were determined from the constructed absorbance-pH curves at the selected wave length as shown in Figure (1) applying the half height method [19]. From this method the pK values are obtained by relations(1,2). The pk (at $A_{1/2}$) was calculated from absorbance-pH curve in Figure (2). The results obtained are given in Table (2)

.

Table 2 : Spectrophotometric determination of ionization and protonation constants of azo dye

pK_p	pK_{a1}	pK_{a2}	λ_{max} (nm)
3	10	7.5	430

pK_p= Protonation of the nitrogen atom.
pK_{a1}= Ionization of the OH–group.
pK_{a2}= Ionization of the second OH–group.

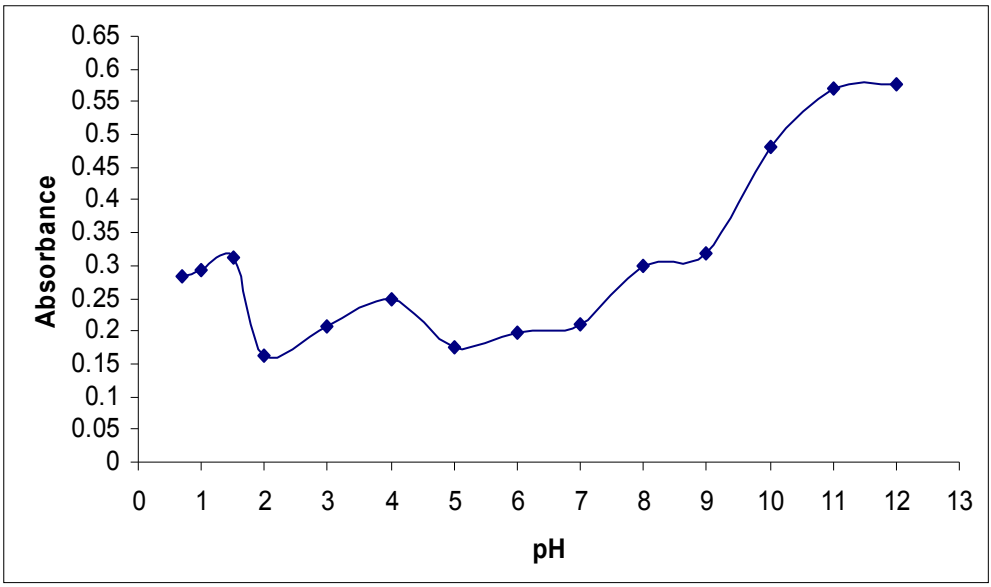


Figure 2. Absorbance – pH curves of Azo compound HyperChem Calculation .

In this work we attempt to study the probable of structure and electronic properties, relative stabilities for the azo dye with and without intramolecular hydrogen bonding. The geometries of the molecules were optimized first by using the molecular mechanics (MM+) force field, where the lowest energy conformations are obtained. The final optimized geometries were obtained by performing the semi-empirical molecular orbital theory at the level of the AM1 of theory. The optimized geometries are shown in fig .4.this figure illustrates the geometry of the molecules in the sticks model[23-25].

Table 3; Present some of the optimized calculated total energies and dipole moment, binding energy and semi-empirical heats of formation of the molecules under study .

The total energy in a molecular orbital calculation is the net result of electronic kinetic energies and the interaction between all electrons and atomic cores in the system[26]. On the other hand the heat of formation of configuration (I,II) of azo dye are exothermic. The configuration II of azo dye has the smaller value of heat of formation (-233.910141kcal/mole). So , according to these results it is thermodynamically more stable than the configuration I of azo dye. Also the dipole moment values are also considered for locating the coordination site. When dipole moment values are changed, like that in case of different metals then net increase in electronic charge is observed. Table 3 present four molecules orbitals energy : the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The values of the difference between the HOMO and LUMO orbitals, known as energy band gap (ΔE), are also given in table 3 the compound (II) more stable than compound (I) because of have high energy gap ΔE, in addition according to this principle the minimum energy system has high energy gap ΔE value. Hence, energy gap ΔE is a qualitative tool to study the stability of the system. So that from table 3, it is obvious that the compound (II) have minimum total energy and maximum energy gap ΔE. There for the compound (II) more stable than compound (I) because of configuration II of azo dye possible forming the intermolecular hydrogen bonding which causes high stabilities[27-30].

Table 3: Calculated Total energy, Binding, Heat of formation in kcal/mol and The MO energy of HOMO, LUMO levels, ΔE(in eV) and the dipole moment μ(in Debyes) .

Azo dye	Total energy	Heat of formation	HOMO	LUMO	ΔE	Dipole (debye)
I Without IHB	-171939.1563	-233.7513123	-9.356372	-1.943541	7.41283	6.903
II With IHB	-171939.3125	-233.910141	-9.304711	-1.611551	7.69316	6.925

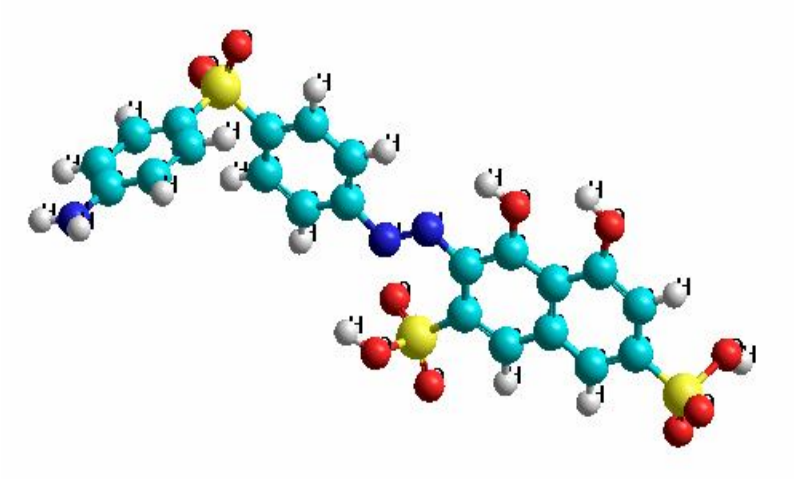


Figure 5. Semi-empirical AM1 calculated optimized structure of configuration of azo dye without intramolecular hydrogen bonding (I) of the possible geometry of azo dye under study in gas phase

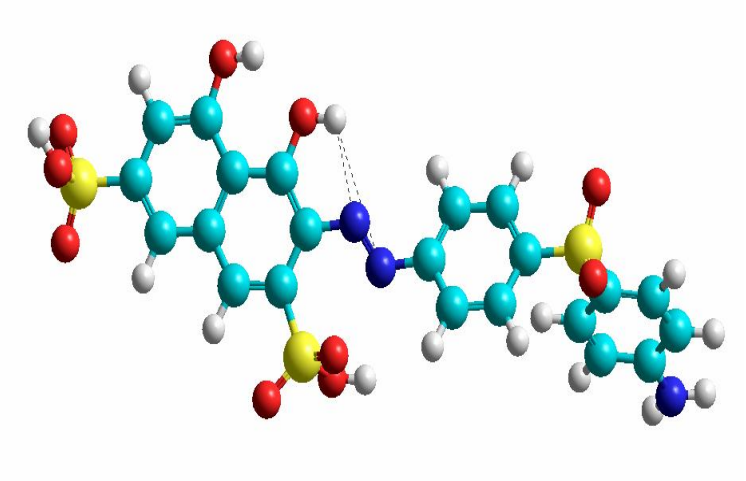
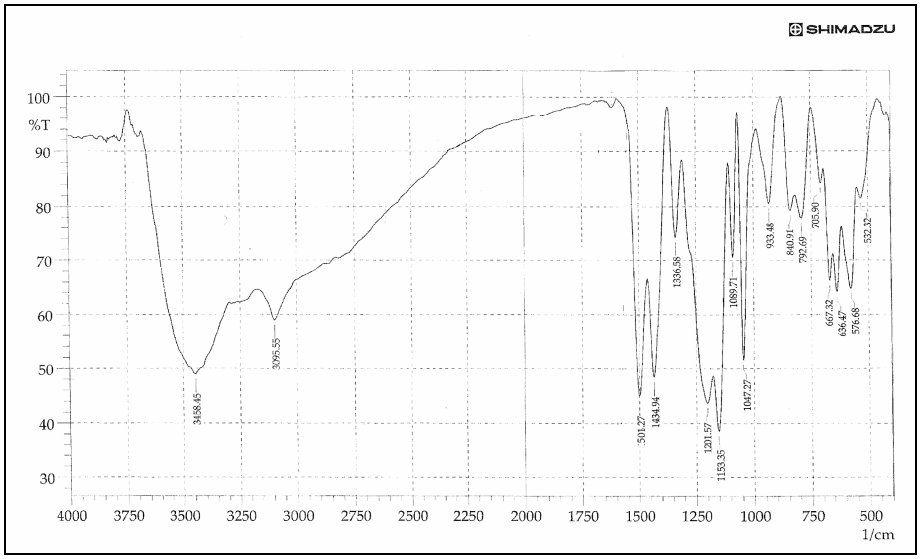


Figure 4. Semi-empirical AM1 calculated optimized structure of configuration of azo dye with intramolecular hydrogen bonding (II) of the possible



geometry of azo dye under study in gas phase.

Figure 5. IR spectrum of azo dye

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الخلاصة:تم في هذه البحث تحضير صيغة آزوية جديدة مشتقة من حامض الكروموتروبك مع المركب 4,4–سلفونايل ثنائي الانلين بطريقة فوكس. شخصت الصبغة المحضرة بواسطة طيف الأشعة تحت الحمراء طيف الأشعة المرئية وتحليل الدقيق للعناصر.وقد تمت دراسة تأثير الأس الهيدروجيني في أطياف الأمتصاص الألكترونية للصبغة المحضرة في المنطقة المرئية بمدى من الاطوال الموجيةnm(360-650) وبأستعمال محلول منظم ذو قيم أس هيدروجيني مختلفة ومن هذه الأطياف تم حساب ثابت تأين مجموعة الهيدروكسيل وثابت برتنة النايتروجين باستخدام طريقة منتصف الارتفاع .فقد وجد تقارب كبير في قيم ثابت تأين لمجموعة الهيدروكسيل. أضافة الى ذلك تم في هذا البحث دراسة نظرية للخصائص والصفات التركيبية والالكترونية للصبغة ألازوية بوجود التاصر الهيدروجيني الضمني وبعدم وجوده بواسطة كيمياء الكم لأول مرة . موائمة التراكيب انجزت اولا بطريقة (MM+)ومن ثم أكملت الموائمة الهندسية بطريقة الشبه تجريبية المستوى الثالثAM1 . اظهرت الدراسة ان صبغة ألازو بوجود التأصر الهيدروجيني الضمني أكثر استقرارا ، وكما تم حساب حرارات التكوين ،ا لعزم ثنائي القطب ، طاقة الاوربيتال الجزيئية HOMO LUMO, وقيمة ΔE