The Preparation, Characterization and the Study of the Linear Optical Properties of a New Azo Compound

[1]Hasanain A S. A Majeed, [2]Alaa Yassin Al-Ahmad and [1]Kawkab Ali Hussain
[1]*Department of Chemistry*
[2]*Department of Physics – College of Education – Basrah University .*
Basrah – Iraq

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Abstract

Azo dye was prepared from 4,4-diaminodiphenyl sulfone with chromotrpic acid by fox method. Azo dye was identified via IR-Infrared spectrophotometer, UV-visible spectroscopy and elemental analysis (CHN). The basic optical properties of azo dye have been studied at room temperature. The optical energy gap was estimated from the absorption coefficient values using Taue's procedure. The values of the static refractive index $(n_\circ)$, the static dielectric constant (ε_o), oscillator energy (E_o), dispersion energy (E_d), the moments of optical dispersion spectra, and the band gap energy (E_g) have been determined by the Wimple-Didomenico method .

Key words: Azo dye, Band gap energy, Refraction index, Oscillator parameters.

Introduction

The discovery of diazo compounds occurred around the year 1858, which parallels the beginning of what is considered the starting point of modern organic chemistry[1]. Azo dyes contain one or more azo groups (- N =N -) which are linked to SP^2 hybridized carbon atoms, based on the number of such groups [2]. The synthesis of most azo dyes involves the 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]. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups [4]. Azo dyes can be classified either according to chemical guideline (characteristic chemical groups) or by color aspects (application in dye works) [5]. Azo dyes are the most important class of industrial dyes, both in number and amount, in dyeing wool, semiconductivity textile and food industries [6-9]

In the present study azo compound were prepared and Identified by IR, UV–Visible spectroscopy and elemental analysis (CHN). The optical constants of the sample are determined by optical characterization method.

[2]**corresponding author.**
E-mail address: alaa_ta2005@yahoo.com

Experimental

Reagent

Methanol, 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 [10]. Physical measurements, IR spectra were recorded on a Buck Scientific Model 500. IR spectrophotometer using a KBr disc in the range (4000 – 600) cm^{-1}. Absorption Spectra in Methanol were determined on a U-1500-HITACH UV-visible spectrophotometer in the range (300-900nm). The melting point (MP) of the compounds was determined with a 9300 Model – Electro thermal melting point. IR, UV-visible spectrophotometer and melting point was performed by Chemistry Department – Education College – Basrah University. Elemental analysis (CHN) of the compounds was determined with (Euro Vector EA 3000A Italy) was performed by AL-al-bayt university.

Methods

Synthesis of the Azo Dyes

The above azo dyes were prepared by a method similar to that described by Fox [11]. In the present method the dyes were prepared as the follows:

1. (0.006mole, 1.4898g) of amine was dissolved in 2ml of conc. HCl and then 10ml of distilled water was added, the mixture was stirred and kept in ice bath.
2. 0.456g of $NaNO_2$ was dissolved in about 5ml of distilled water and kept in ice bath.
3. Diazonium salt was prepared by adding sodium nitrite solution in step (2) dropwise to the cold solution of amine in the step (1) with stirring and kept the temperature below 50 ^oC.
4. Coupler was prepared by dissolving (0.006mole, 2.4017g) of chromotropic acid disodium salt dehydrate in 25% sodium hydroxide solution and keeping in ice bath.
5. The diazonium salt was added dropwisely to the couplers with constant stirring, keeping the temperature below 50 ^oC; the dyes were neutralized with dilute hydrochloric acid solution.
6. The resulting crudes were recrystallized from methanol the purity of the resulting azo dye, 94% yield , M.P. >300 ^oC , orange color. Azo dye has been characterized by elemental analysis, IR, and UV spectra. The structure of the azo dye is shown in figure 1.

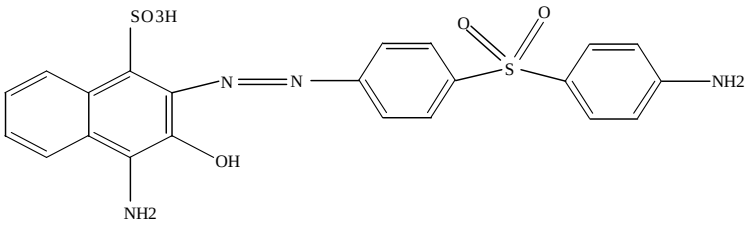

Figure 1. chemical structures of the prepared azo dye compound

Result and Discussion

In this paper, we describe the synthesis of azo dye from 4,4-diaminodiphenyl sulfone with chromotrpic acid, were formed in good yield, and it's stable at room temperature and are nonhygroscopic. The structures of the compositions of the prepared azo dye were determined by elemental analysis for C, H and N. The obtained results are shown in Table 1. A reasonable agreement between the found and calculated data was found. The azo dye was identified by IR spectroscopy in the range (4000–600) cm^{-1} as KBr discs is shown in Figure 4. The stretching vibration of the OH groups which appeared in the region (3300-3450) cm^{-1}. 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. Also azo dye shows two absorption bands (3300 – 3410) cm^{-1} which may be attributed to the ν (-NH2) group, which overlaps with the stretching vibration of the OH groups. The band corresponding to N=N stretching vibration usually lies around 1500 cm^{-1} [12], the C=C stretching vibration of the aromatic ring shows a strong band in the region (1590) cm^{-1}, stretching vibration of the (C-H) aromatic appear at (2900) cm^{-1} [13-14] . The all mentioned bands were shown in table1.

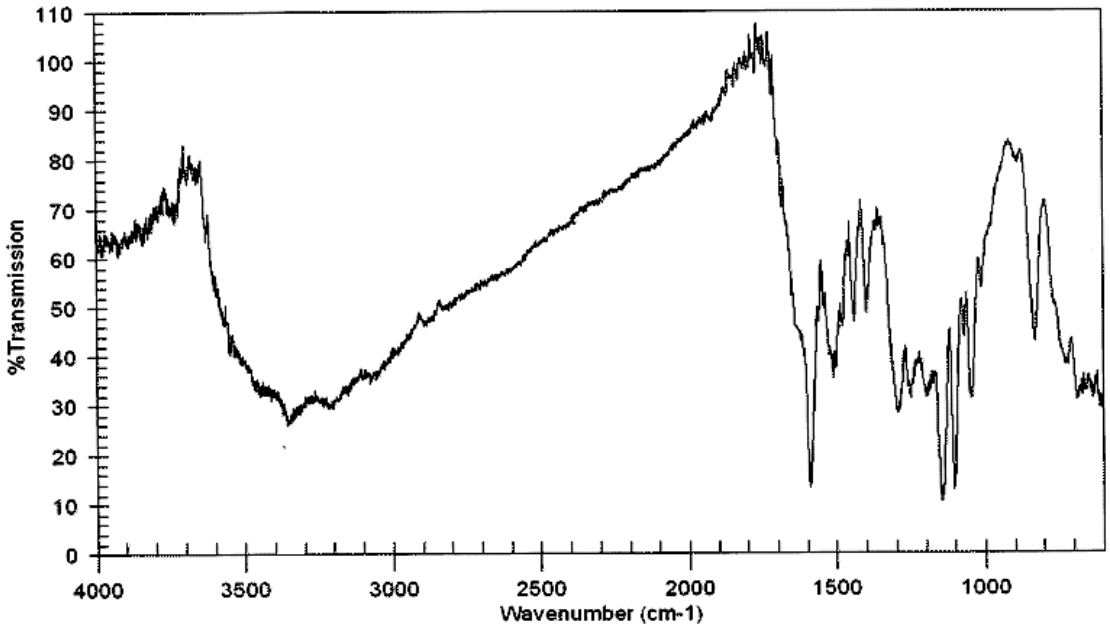

Figure 2. IR-spectrum of azo dye

Table 1. IR and C.H.N data for azo dye compound
(Br:broad, s:sharp, m:medium, w:weak)

Compound	Wave numbers (cm^{-1})					Calculated (Found)(%)		
	υ O-H m	**υ C=C m**	**υ N-H br**	**υ N=N s**	**υ C-H m**	**C**	**H**	**N**
Azo dye I	**3300-3450**	**1590**	**3300 – 3410**	**1500**	**2900**	**52.93 (53.00)**	**3.55 (3.63)**	**11.01 (11.23)**

Linear Optical Properties:

Azo dye has received great attention due to its environmental stability, ease of preparation, and its optical and electrical properties. Optical properties of any azo dye are important for optical applications, because optical properties are directly related to their structural and electronic properties [15].

Linear optical properties have been the subject of numerous investigation by both theoreticians and experimentalists in recent years due to the potential applications in optical signal processing and computing [16]. Detailed investigation of linear optical coefficients is ables to fabricate materials, appropriately designed at the molecular level for specific applications such as optoelectronic devices. Knowledge of optical constant of the materials (optical band gap and extinction coefficient) is vital to scrutinize the atomic structure, electronic band structure and electrical properties. The refractive index provides the information about the chemical bonding and electronic structure of the material [17].

Sample Preparation and Optical Measurements

The azo dye film used in the present study was prepared as follows: (0.5*gm*) of azo dye powder was dissolved in (10 *ml*)ethanol, the dye solution was stirred at room temperature for 45min, then the solution is filtered through (0.2μm)syringe filter. The film was prepared by the repeat- spray method on a clean glass slide substrate of (25 mm×25 mm×1 mm) in size that is heated up to 70 ^{o}C. Smooth film without dust and solvent residues was obtained. The thickness of the film is about (30 μm), and the film samples have good purity and uniform thickenss.

UV-visible spectroscopy has been used to characterize the sample in the spectral range (300-900 nm) in steps of 2 nm. The transmittance (T) and the absorbance (A) of azo dye measurements using double beam UV-Visible spectrophotometer (U-1500- HITACH). These measurements were performed at room temperature. Fig.(1) shows the spectral distribution of absorbance for azo dye film in the spectral range (300-900 nm), figure 3 shows that the peak of absorption is located at 305 nm.

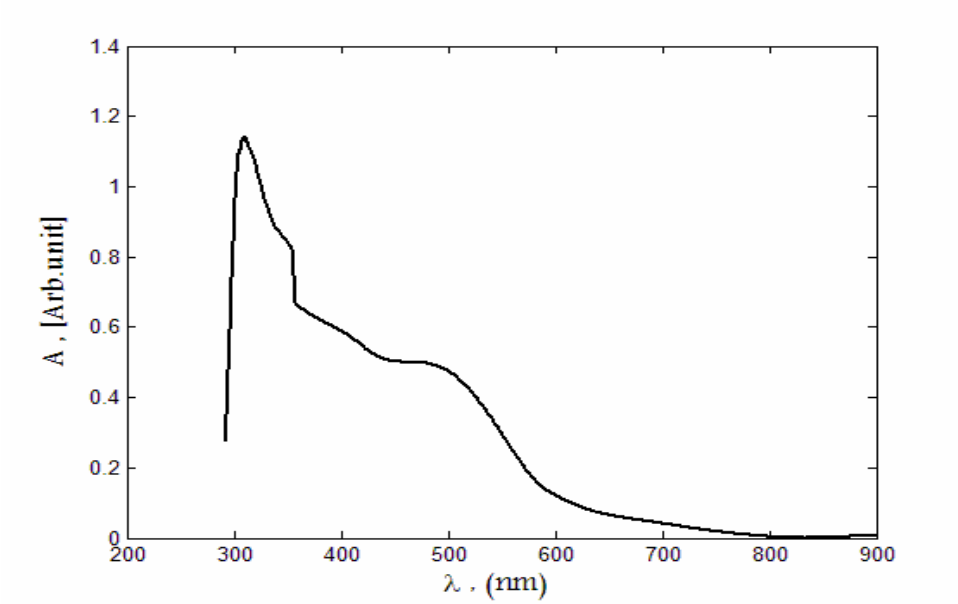

Figure 3. Absorption spectra of azo dye film

The analysis of optical transmission spectra is one of the most productive tools for understanding and developing the band structure and energy band gap of materials. The spectral dependence on transmittance (T) and reflectance (R) for azo dye is given in figure 4.

The reflectance was calculated using the following equation [18]

$$T = (1-R)^2 \exp(-\alpha d) \qquad (1)$$

Where d is the cell path length and (α) is the absorption coefficient.

From the transmittance and the reflectance spectral of azo dye we can see that at a large wavelength (λ >800 nm) the azo dye shows high transmission. The in quality(R+T<1) at wavelength (λ < 800 nm) implies the existence of absorption, i.e. an absorbing region.

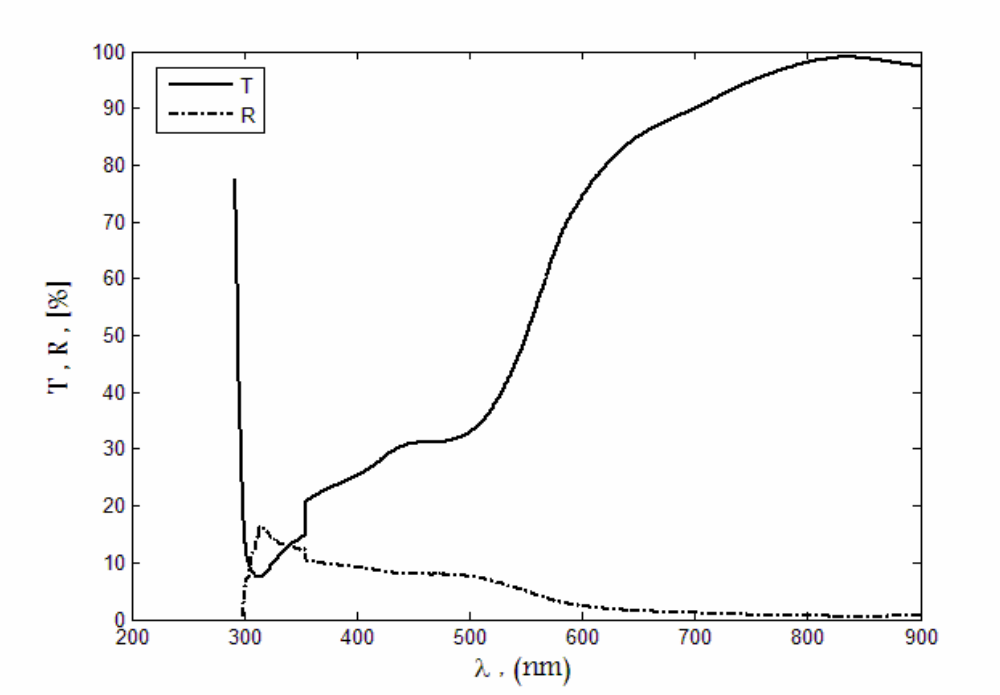

Figure4. The spectral distribution of transmittance (T) and reflectance (R) as a function of wavelength for azo dye film .

The refraction index (*n*) and extinction coefficient (*k*) provides the optical properties of the azo dye and the are related by [19].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - k^2\right)} \qquad (2)$$

The absorption coefficient (α) can be calculated from the transmittance spectral data using Beer Lamber's formula $(\alpha = 2.303(A/d))$, where A is the optical absorbance of the dye. The extinction coefficient (*k*) can be obtained from the relation $(k = \alpha\lambda/4\pi)$, where λ is the wavelength of the light.

Figure 5 and 6 show the variation of the refraction index and extinction coefficient as a function of wavelength. From the figures we can see that the values of refractive index (n) and extinction coefficient (k) in the region of (305-600nm) are sharply decreases with increasing of the wavelength. In the region (600-900nm) the values of n and k decreases gradually. This is due to high energy transition.

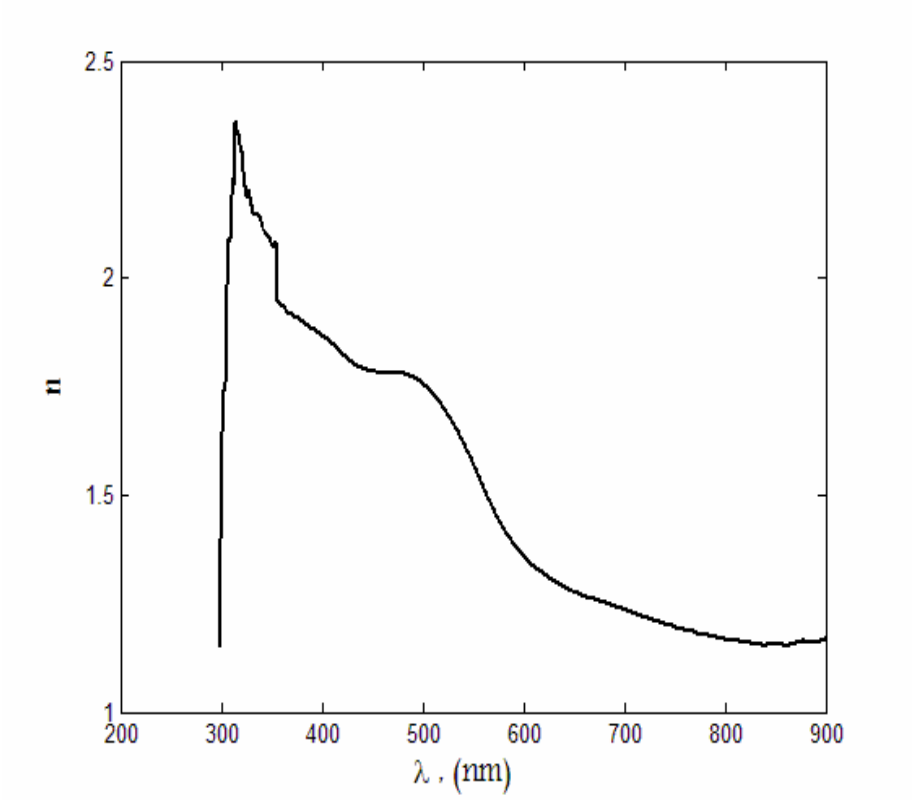

Figure 5. Refraction index as a function of wavelength for azo dye film.

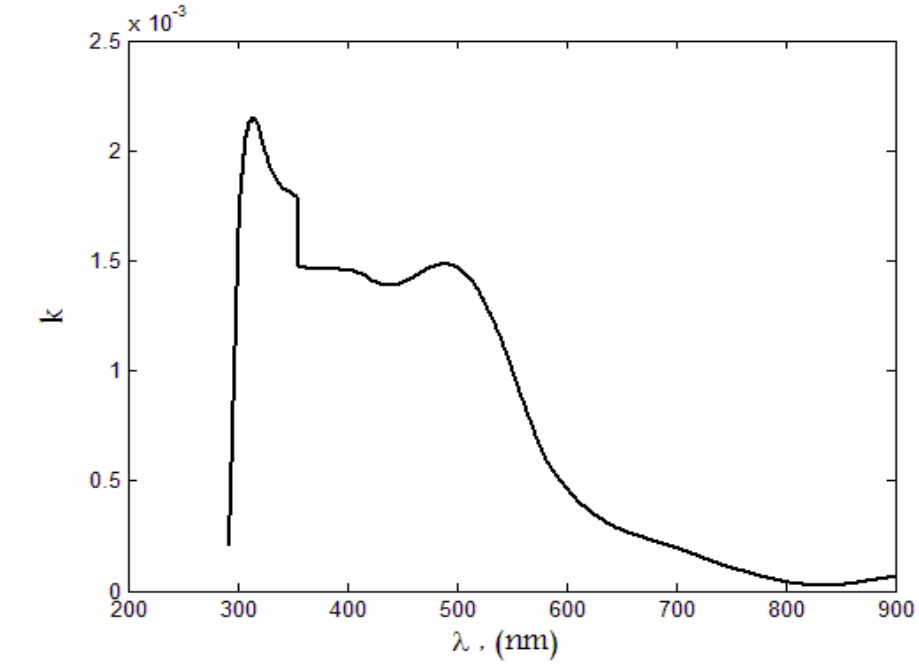

Figure 6. Extinction coefficient as a function of wavelength for azo dye film.

By employing the Wemple-DiDomenico single oscillator model [20] in the region of normal dispersion (λ > 300nm), we analyz the measured refractive indices and the data are then used to obtain the oscillator parameters. Equations (3) describes the relationship between the refractive indices and the oscillator parameters.

$$\frac{1}{(n^2-1)}=\frac{E_o}{E_d}-\frac{E^2}{E_o E_d} \qquad (3)$$

Where ($E = h\upsilon$) is the photon energy, h is the Planck constant, υ is the photon frequency, (E_o) is the average excitation energy for electronic transitions and (E_d) is the dispersion energy which is a measure of the average strength of inter-band optical transitions or the oscillator strength. Figure 7 shows the plotting of $(n^2-1)^{-1}$ against $(h\nu)^2$ which allows us to determine the oscillator strength parameters by fitting a linear function to the lower energy data. The point of interception with the ordinate at $(E(h\nu)^2=0)$ yields the value of dielectric constant at higher wavelength (ε_∞). The values of (E_o) and (E_d) are obtained from the intercept and the slope of the curve and the static refractive index $(n_\circ)$ is calculated using this relation $n^2(h\nu=0)=\frac{E_d}{E_\circ}+1$.

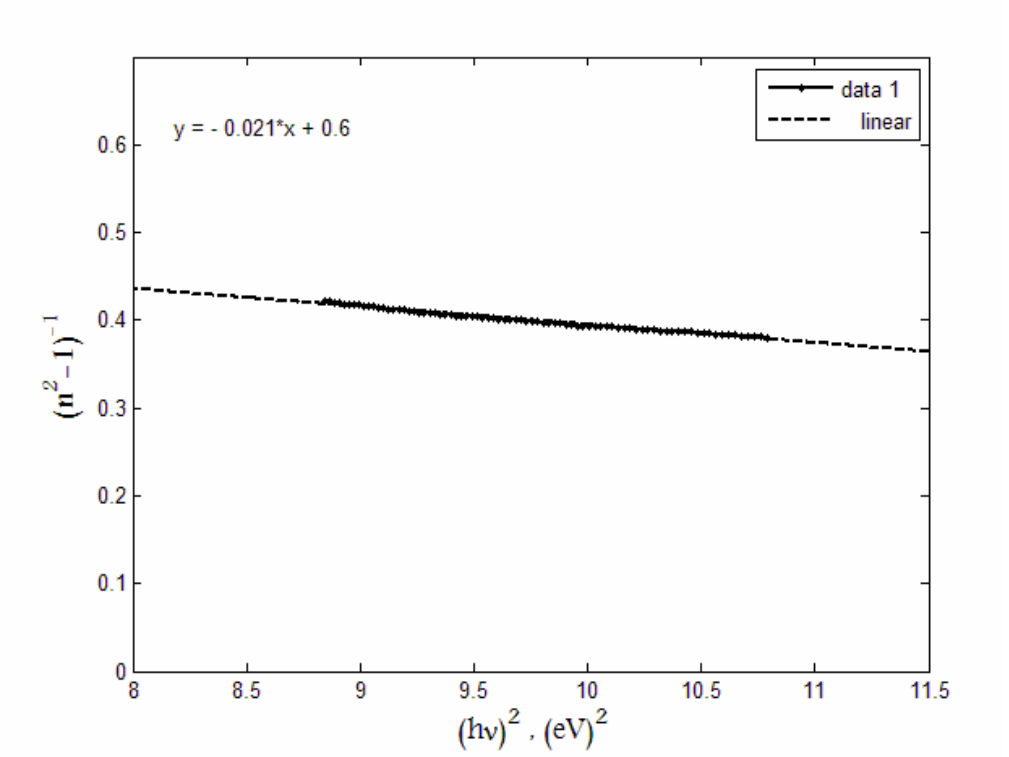

Figure 7. Variation of (n^2-1) versus $(h\nu)^2$ for azo dye film.

The moments of optical dispersion spectra M_{-1} and M_{-3}, can be evaluated using the relations [20].

$$E_\circ^2=\frac{M_{-1}}{M_{-3}} \qquad (4)$$

$$E_d^2=\frac{M_{-1}^3}{M_{-3}} \qquad (5)$$

The variation in the absorption coefficient (α) is related to the photon energy $h\upsilon$ for the inter-band transition by the relation [21]

$$\alpha h\upsilon = B(h\upsilon - E_g^{opt})^r \quad (6)$$

Where (r=1/2) and (2) in the case of direct and indirect optical transition respectively, $h\upsilon$ is the photon energy, B is the band tail parameter and (E_g^{opt}) is the optical band gap. Figure 8 shows the direct allowed transition (r=1/2). Extrapolating the linear part towards lower photon energies, the point of interception with $h\upsilon$ axis at $((h\upsilon)^2 = 0)$ giving the corresponding direct energy band gap (E_g^d).

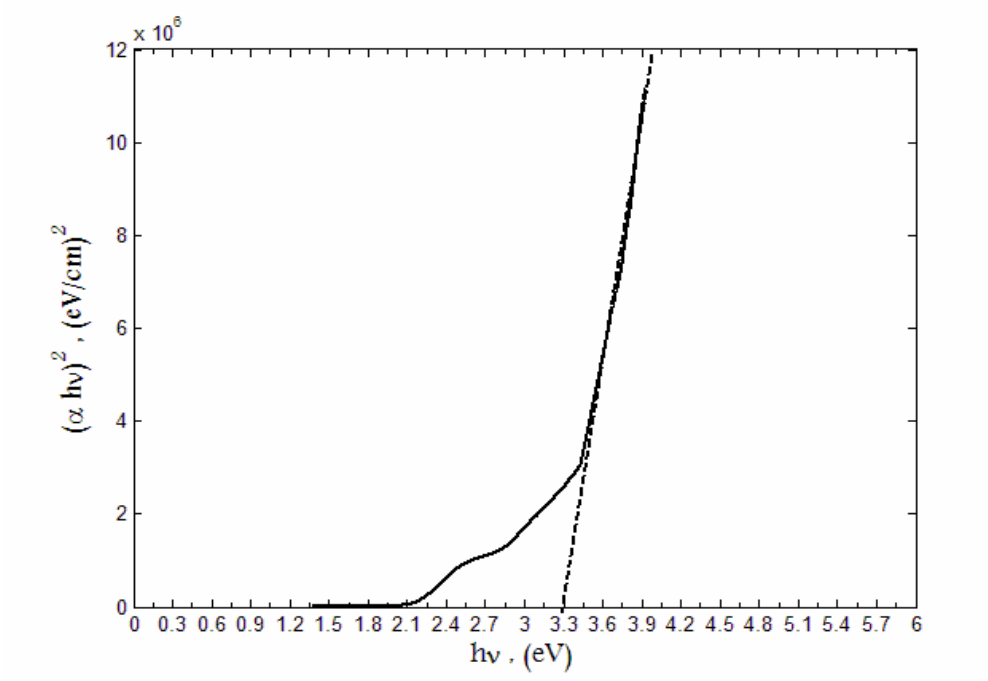

Figure 8. Dependence of $(\alpha h\upsilon)^2$ on the photon energy.

The values of the static refractive index $(n_\circ)$, the static dielectric constant (ε_o), oscillator energy (E_o), dispersion energy (E_d), the moments of optical dispersion spectra M_{-1} and M_{-3}, and direct energy band gap (E_g^d) are listed in table 2.

Table 2. Optical constant of azo dye film.

$n_\circ$	ε_o	$E_\circ(eV)$	$E_d(eV)$	$E_\circ E_d(eV)^2$	$M_{-1}(eV)^2$	$M_{-3}(eV)^2$	(E_g^d)	$\frac{E_\circ}{E_g^d}$
1.63	2.66	5.34	8.90	47.52	1.66	0.0583	3.3	1.61

Conclusions

Azo dye compounds has been synthesized from from 4,4-diaminodiphenyl sulfone with chromotrpic acid. The azo dyes were investigated by infrared spectra and C.H.N analysis. Optical transmission and absorption spectrum is used to calculate the optical absorption coefficient, refractive index , extinction coefficient , optical band gap and oscillator parameters. The UV-visible spectroscopic studies shows that the new Azo compound has high refractive index and high value of static dielectric constant.

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الخلاصة:

تم في هذه الدراسة تحضير مركبات أزو جديدة ومن ثم جرى تشخيص المجاميع الفعالة باستخدام تقنيات عدة. درست الخواص البصرية للمركب الجديد بهدف التعرف على طبيعة منحني الامتصاصية والنفاذية والانعكاسية. استخدمت البيانات المستحصلة من القياسات في حساب الثوابت البصرية الخطية المختلفة وكذلك تم حساب معامل الانكسار ودراسة تغير قيمته نسبة الى التغير في الطول الموجي للضوء الساقط على العينة.أظهرت نتائج القياسات ان صبغة الأزو المحضرة ذات معامل انكسار عالي وكذلك ذات فجوة طاقة عالية نسبيا. أن فجوة الطاقة الضوئية لهذه الصبغة هي ضمن حدود فجوة الطاقة لاشباه الموصلات.