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PREPARATION AND STUDY OF THE ELECTRICAL AND OPTICAL PROPERTIES OF A NEW AZO DYE (4-ACETAMINOPHENOL – [2-(4-AZO)]-4-AMINO DIPHEYL SULFONE)

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The electrical and optical properties of a new azo dye powder (4-Acetaminophenol – [2-(4-Azo)]-4-Amino dipheyl sulfone) have been investigated. The dielectric constant ε' and dielectric loss ε'' depend on the frequency up to 50 KHz and are nearly constant beyond. The optical constants such as refractive index n , the dispersion energy E_d , the oscillation energy E_o , lattice dielectric constant ε_L , the light frequency dielectric constant ε_∞ , the ratio of carrier concentration to the effective mass N/m* and energy bang gap E_g have been determined by reflection spectra in the wavelength range (200-1100) nm. The nonlinear properties and thermo-optic coefficient of this azo dye dissolved in ethanol using Z-scan technique is also investigated.

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Keywords: Electrical properties; Optical constants ; Z-scan, Azo dye

1. Introduction

Azo dye has received great attention due to its environmental stability, ease of preparation, and its optical and electrical properties. Much work has been carried out on the molecular design, synthesis, and assembly of structures with desired properties [1-3]. Knowledge of optical constants of a material such as refractive index and extinction coefficient are quite essential to examine material's potential opto-electronic applications [4]. Further, the optical properties may also be closely related to the material's atomic structure, electronic band structure and electrical properties.

In this paper, the dielectric constant ε' and dielectric loss ε'' have been measured for a new azo dye powder (4-Acetaminophenol–[2-(4-Azo)]-4-Amino dipheyl sulfone) in the frequency range ($100 - 2\times10^6$) Hz . The optical constants of the azo dye powder discs of 1cm diameter are determined by optical characterization method, also, the nonlinear optical properties for the azo dye in the ethanol solution were investigated by the use of the Z-scan technique.

2. Experimental details

2.1 Sample preparation

An azo dye was prepared by a method similar to that described by Fox [5]. In the present method the dye was prepared as follows

1.(0.006 mol, 1.4898 g) of the amine was dissolved in 2 ml of concentrated HCl and then 10 ml of distilled water was added, then the mixture was stirred and kept in an ice bath.

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2. 0.456 g of $NaNO_2$ was dissolved in about 5ml of distilled water and kept in an ice bath.

3. Diazonium salt was prepared by adding sodium nitrite solution in step (2) drop wise to the cold solution of amine in the step (1) with stirring and keeping the temperature below5 ^0C .

4. A coupler was prepared by dissolving (0.006mole, 1.4355 g) of 4-acetaminophenol in 25% sodium hydroxide solution and keeping it in an ice bath.

5. The diazonium salt was added drop wise to the couplers with constant stirring, keeping the temperature below 5 ^0C , the dyes were neutralized with dilute hydrochloric acid solution.

The solid product was collected and recrystallized from methanol. The yield of reaction was 94% , its colour was orange, and the melting point was 272 ^0C .

The azo dye has been characterized by the elemental analysis (CHN), IR and UV spectra. The azo dye powder was pressed under pressure of 7 tons/cm^2 into small discs of 1cm diameter using evacuated press. The chemical structure of the chosen azo dye compound is shown in Fig.1.

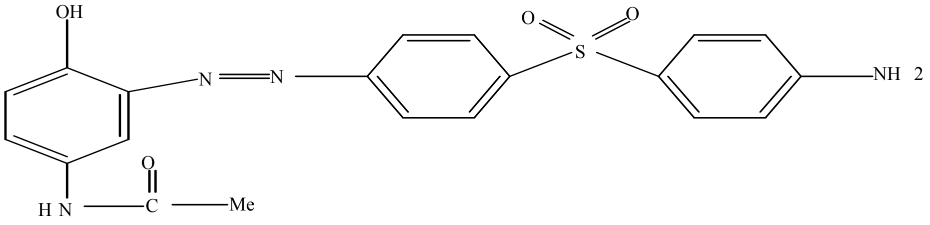

Fig.1. Chemical structure of the azo dye

2.2 Infrared spectrum

The azo dye powder was identified by IR spectroscopy in the range (4000–500) cm^{-1} as shown in Fig.2.

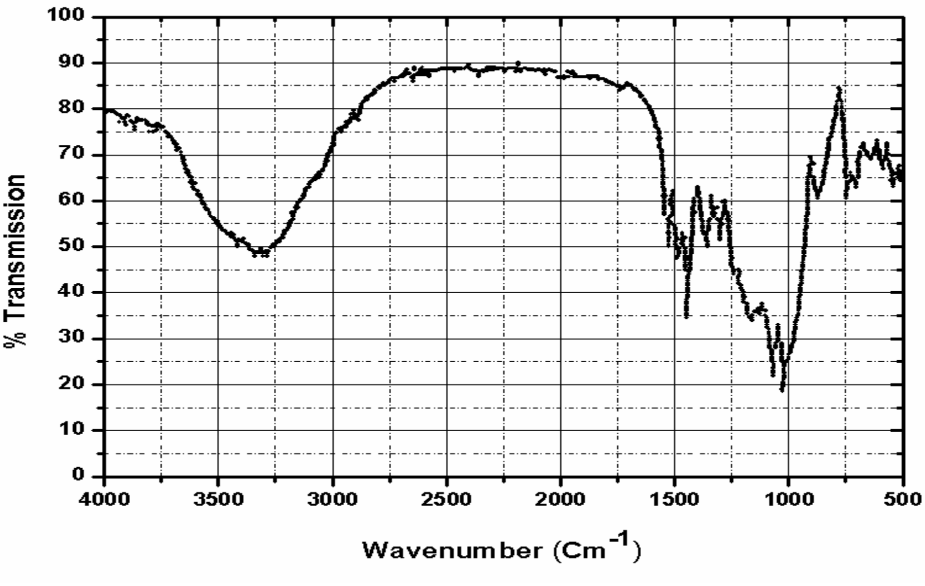

Fig.2. IR-spectrum of azo dye.

The stretching vibration of the OH group which appeared in the region of (3125-3595) cm^{-1} cancels the absorption peak of ($-NH_2$) group supposed to appear at same region. The band shows broad appearance due to its relatively low frequency. It can be concluded that the (-OH) group may form a hydrogen bonding with nitrogen atom. The band corresponding to (-N=N-)

stretching vibration usually lies around (1445)cm^{-1}[6], the (-C=C-) stretching vibration of the aromatic ring cited at (1530) cm^{-1}. Stretching vibration of the (-C-H) aromatic appears at (3025) cm^{-1}. The all mentioned bands are given in Table 1.

Table 1. IR and CHN data for azo dye compound.

Wave numbers (cm^{-1})				Calculated (Top) (Found)%(Bottom)		
ν O-H & ν N-H	ν C=-C	ν N=N	ν C-H	C	H	N
3125-3595	1530	1445	3025	57.27 (57.23)	4.55 (4.34)	14.06 (13.98)

3. Results and discussion

3.1 Dielectric measurements

Capacitance and dielectric loss measurements were performed on azo dye using an RLC model (METRAWATT) with range (1nF-1μF), EM 1634 function generator and conventional two terminals sample holder. Dielectric permittivity measurements were carried out on sample thickness of 0.089 cm and examined area was 50.24x10^{-4} cm^2. The sample was covered with a film of silver paste on opposite surfaces to obtain good metal contact and was placed inside a dielectric cell whose capacitance was measured at room temperature for different frequencies. The technique used for the measurement of dielectric constant is reflection coefficients or resonant frequencies. In the later case, material is characterized to a loaded resonant cavity and the sample permittivity is evaluated from the shift of the resonance frequency value, compared to that of the empty (un- loaded) cavity. The dielectric constant was calculated using the following relation [7]:

$$\varepsilon' = C_p d / A\varepsilon_0 \tag{1}$$

where ε_0 is the permittivity of free space, d and A are the sample thickness and area, and C_p is the parallel capacitance.

The dielectric loss ε'' was calculated using the relation [8]:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{2}$$

where $\delta = 90 - \Phi$, Φ is the phase angle. The observations were made in the frequency range $(100 - 2\times10^6)$Hz at room temperature. Dielectric measurements of the sample are shown in Fig.3 (a and b). From the total behaviour we can notice that the dielectric constant and dielectric loss decreases with increasing frequency (f >50 KHz) and reaches steady state at higher frequencies (f >500KHz).The high dielectric constant value of the azo dye at low frequency is attributed to space charge polarization [9].

In the frequency range (100Hz to 50 KHz) the dielectric constant ε' and dielectric loss ε'' are constants. This is attributed to the fact that dipoles have sufficient time to align with the field before it changes direction and the dielectric constant is high. And also, enhancement of ε' and ε'' values due to interfacial polarization (Maxwell- Wagner - Sillars effect or polarization), it arises from the increased accumulation of electric charges on the structural interface, and has great importance in practical applications of dielectric materials in multi-stage isolators [10]. In principle, at low frequencies and temperature, four different types of polarizations (i.e., electronic, ionic, dipolar and interfacial) contributes to the total value of ε [11]. But at high frequency range (50-500) KHz the contributions of ionic, dipolar and surface polarizations become negligible and the dipoles partially rotate before the field changes its direction therefore ε' and ε'' decrease with increasing frequency corresponding to interfacial polarization only. Then the values of ε' and ε'' become constant with high frequency over 500 KHz since the rotational motion of the polar molecules of dielectric is not rapid enough in comparison with the variation of the field [12].

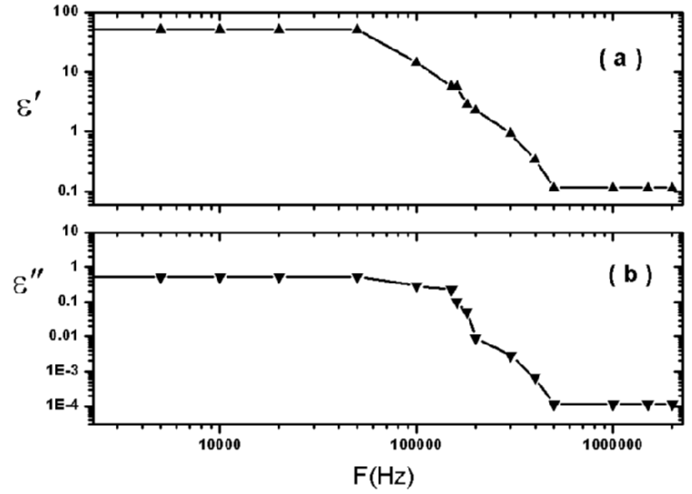

Fig.3. The variation of dielectric constant ε' (a) and dielectric loss ε'' (b) as a function of frequency.

3.2 Optical measurements

For optical measurements, the reflectance R of the sample surface was measured at room temperature by normal incidence of light of wavelength (λ) range (200-1100) nm in steps of 2 nm using Cecil Reflecta-Scan CE -3055 Reflectance Spectrometer, as shown in Fig.4.

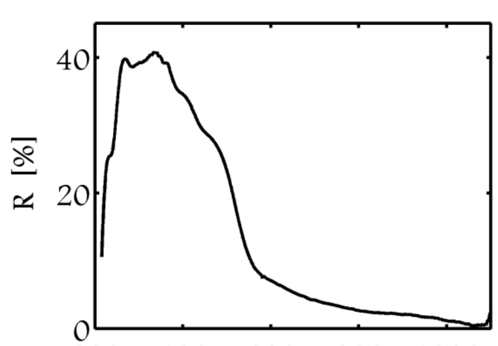

Fig .4. Reflectance as a function of wavelength.

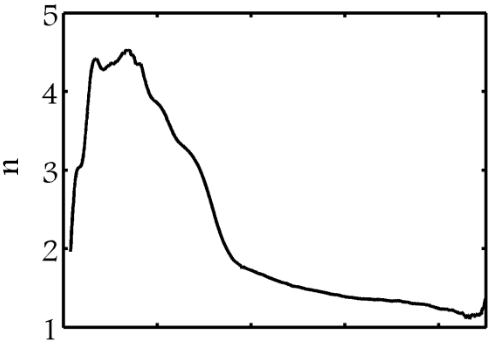

Fig.5. Dispersion curve of the refractive index

The experimental error in measuring the reflectance R was calculated using the following equation [13]:

$$R = \left(\frac{I_r}{I_m}\right) \times R_m \qquad (3)$$

where I_r and I_m are the intensities of light reflected from the sample and the reference mirror respectively, and R_m is the mirror reflectance. The refractive index n was approximately calculated using the following equation [13]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \tag{4}$$

Fig. 5 shows the dispersion curve of the refractive index n in the wavelength range (200-1100) nm. Normal dispersion at λ >700 and anomalous dispersion at λ< 700 are observed.

The relation between the real part of the optical dielectric constant, $\varepsilon_1 (= n^2)$, and wavelength λ is given by the equation [14]:

$$\varepsilon_1 = n^2 = \varepsilon_L - e^2 N / (4\pi^2 c^2 \varepsilon_o m^*) \lambda^2 \tag{5}$$

where ε_L is lattice dielectric constant , c is the velocity of light and e is the electron charge, ε_o the permittivity of the free space. Fig.6 shows the dependence of n^2 on λ^2. Extrapolating the linear part to zero wavelength gives the value of ε_L. The calculated value of the lattice dielectric constant ε_L and the ratio of carrier concentration to the effective mass N/m^* are 2.7 and $2.355 \times 10^{31} (m^3 Kg)^{-1}$ respectively.

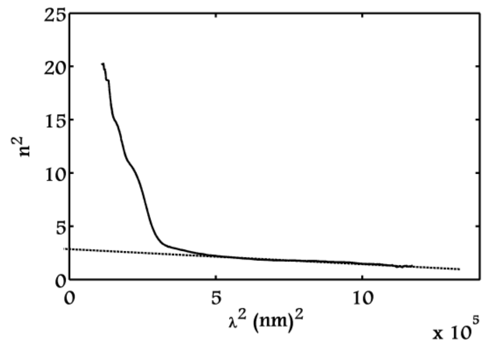

Fig.6. Optical dielectric as a function of λ^2

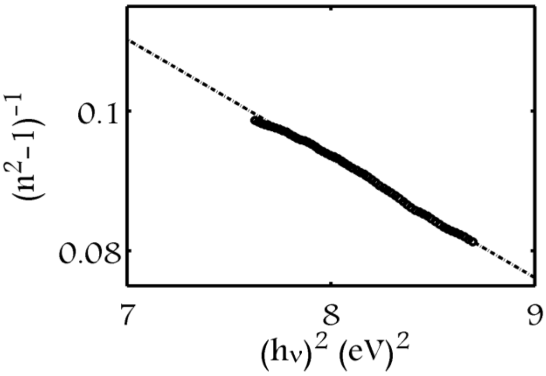

Fig.7. $(n^2-1)^{-1}$ *as a function of* $(h\nu)^2$

The relation between the refractive index n and the oscillator strength below the band gap is given by Wemple and DiDomenico equation [15]:

$$(n^2 - 1)^{-1} = \frac{E_o}{E_d} - \frac{1}{E_o E_d} E^2 \tag{6}$$

where E_o is the oscillator energy, $E = h\nu$ is the photon energy and E_d is the dispersion energy, which measures the average strength of the interband optical transition.

Fig.7 shows the relation between $(n^2 - 1)^{-1}$ and E^2 for the investigated composition. The values of E_o and E_d can be determined from the slope and the intercept. The calculated values of dispersion energy E_d and the oscillator energy E_o are found to be 16.35 eV and 3.59 eV respectively. From the intercept, the high-frequency dielectric constant, $\varepsilon_\infty = n_\infty^2$ equals 2.56 . It is clear that $\varepsilon_L > \varepsilon_\infty$ by 0.14, and this result is attributed to the small concentration contribution of free carriers for polarization. The moments of optical dispersion spectra M_{-1} and M_{-3} can be evaluated using the relationships [15]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad \text{and} \qquad E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{7}$$

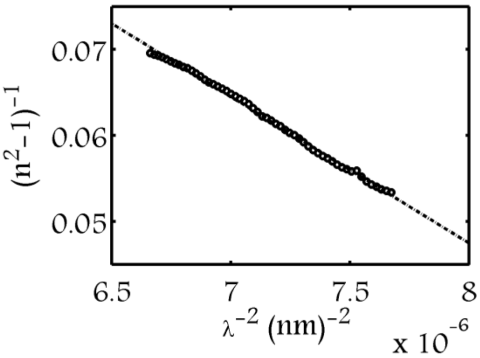

Fig.8. $(n^2-1)^{-1}$ *as a function of* λ^{-2}

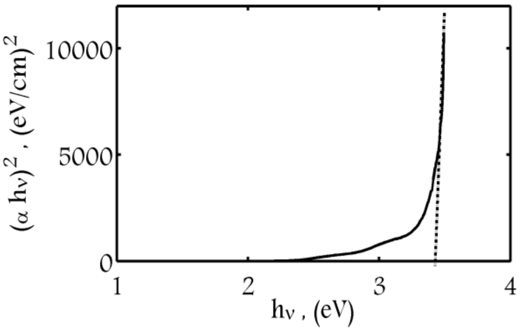

Fig. 9. $(\alpha h\nu)^2$ *as a function of* $h\nu$

The refractive index can also be analyzed to determine the average oscillator wavelength λ_o. This quantity can be obtained using the single term Sellmeier oscillator [16]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \tag{8}$$

From Fig. 8 we obtained λ_o value from the linear part of the relation $(n^2-1)^{-1}$ versus λ^{-2} and is given in the Table 2. Rearranging equation 8 gives [17,18]:

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - (\lambda_0 / \lambda)^2} \tag{9}$$

with introducing $S_0 = (n_\infty^2 - 1)/\lambda_0^2$ as the average oscillator parameter which is the strength of the individual dipole oscillator. The S_0 value for the sample is calculated using equation 9 and is given in Table 2.

For photon energy $h\nu$ falling on the material and assuming direct transitions between the valence and conduction bands, the absorption coefficient is related to the band gap E_g as follows The energy band gap of this component is determined by the reflection spectra. According to the Taus relation, the absorption coefficient, for direct band gap component, is given by [19]:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \tag{10}$$

where C is a constant and α is the absorption coefficient which is given by [20]

$$2\alpha t = \ln[(R_{\max} - R_{\min})/(R - R_{\min})] \tag{11}$$

where t is the thickness of the sample, $R_{\max}$ and $R_{\min}$ are the maximum and minimum value of reflectance, R the reflectance at a given photon energy, $h\nu$. The E_g value was estimated to be 3.43 eV by extrapolating the linear part of $(\alpha h\nu)^2$ versus $h\nu$ in Fig.9.

Wemple and DiDomenico expression can also be used to determine the non-linear effect in optical materials from linear optical index of refraction n. The Millers rule is very convenient for visible and near-infrared frequencies [15], which is equivalent to the third order non-linear polarizability parameter $\chi^{(3)}$ so called non-linear optical susceptibility and linear optical susceptibility $\chi^{(1)}$ through:

$$\begin{aligned} \chi^{(3)} &= A(\chi^{(1)})^4 \\ &= A\ [E_0 E_d / 4\pi(E_0^2 - E^2)]^4 \end{aligned} \qquad (12)$$

where A=1.7x10^{-10} (for $\chi^{(3)}$ in esu). The calculated values of non-linear optical susceptibility $\chi^{(3)}$ according to equation 12 is shown in Fig.10.

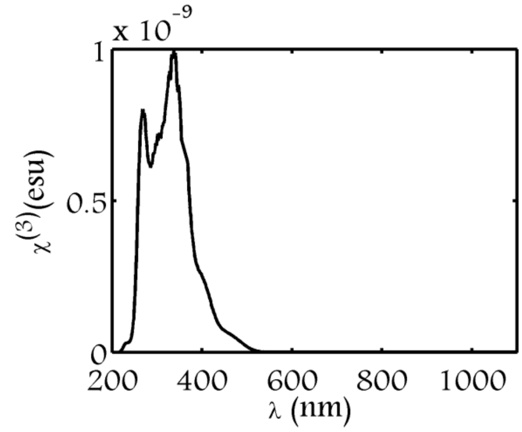

Fig.10. Third order nonlinear optical susceptibility as a of function of wavelength

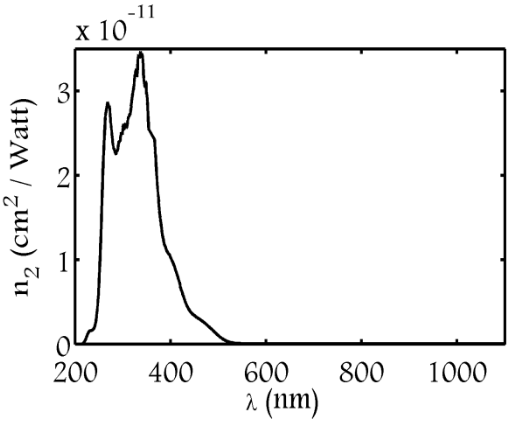

Fig.11.Nonlinear refractive index as a function wavelength

The covalency and ionicity of the chemical bonds strongly influence the magnitude of the nonlinearity. The values of nonlinear refractive index n_2 as a function of wavelength is shown in Fig.11 are calculated from semiempirical relation [21] according to equation 13

$$n_2[esu] = [2.6x10^{-13}(n^2 - 1)^4]/n \qquad (13)$$

where $n_2(cm^2/W) = (8.378/n_o)\times10^{-3}\,n_2(eus)$

Table 2. Optical parameters of (4-Acetaminophenol – [2-(4-Azo)]-4-Amino dipheyl sulfone) dye.

$E_\circ$ (eV)	E_d (eV)	M_{-1}	M_{-3} $(eV)^2$	E_g (eV)	$n_\circ$	ε_∞	ε_L	$\lambda_\circ$ (nm)	$S_\circ$ (m^{-2})	n_2 cm^2/W	χ^3 (esu)
3.59	16.35	4.5455	0.3512	3.43	1.6	2.56	2.7	369.27	3.33 $\times10^{13}$	3.98 $\times10^{-15}$	4.03 $\times10^{-14}$

4. Nonlinear optical properties

The nonlinear response of (4-Acetaminophenol – [2-(4-Azo)]-4-Amino dipheyl sulfone) was characterized using the Z-scan technique [22]. This technique employs a single Gaussian laser beam in a tight focus geometry to measure the transmittance of a nonlinear medium as a function of the sample position [23]. The transmittance is measured through a finite aperture in the far field as the sample is scanned along in the Z-direction through the focus of a lens. When the sample is thin enough i.e. less than the Raleigh range, the changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected.

To determine the nonlinear absorption coefficient of the azo dye in the ethanol solution, the sample was first scanned with the open aperture (S=1) as shown in Fig.12(a). The curve is nearly symmetrical and has a minimum at z=0, which is in agreement with the two photon absorption process.

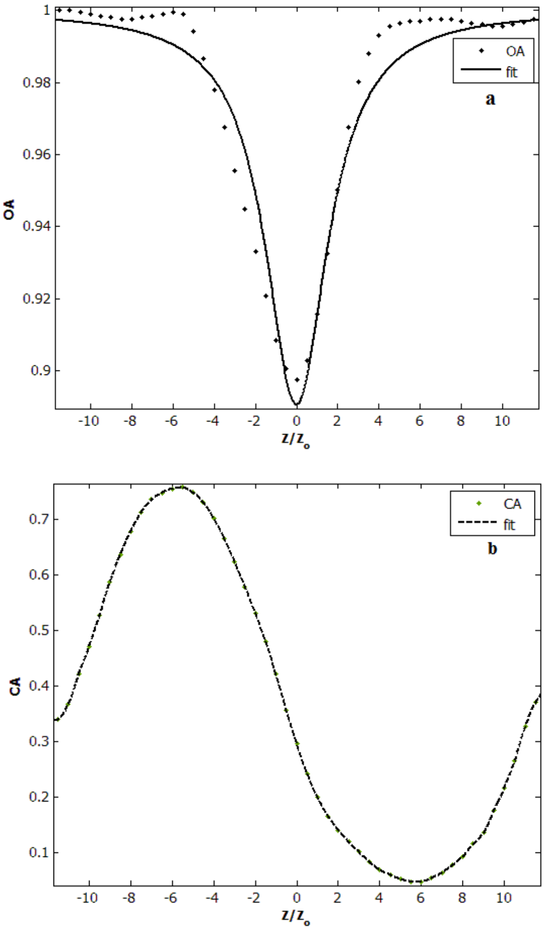

Fig.12. Z-scan experimental data (square) for azo dye solution: (a) open aperture (OA) and (b) closed aperture (CA), solid (dash) line shows theoretical fit to the experimental data.

Fig.12 (b) shows the Z-scan measurement data with the closed aperture, which contains both contributions from the nonlinear absorption and the nonlinear refraction index at incident intensity $I = 5.44\, kWatt / cm^2$. A signature of peak-valley indicating a negative type of nonlinearity from closed aperture (self-defocusing occurs) and two photon absorption type behaviour for open aperture scan was observed.

The change in the refractive index Δn can be evaluated by use of the difference in the peak - valley normalized transmittances, ΔT_{p-v} , which is given by [22]:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} \left|\Delta\Phi_{\circ}\right| \tag{14}$$

where $\Delta\Phi_{\circ}$ is the on-axis phase shift at the focus. The on-axis phase shift is related to the third order nonlinear refractive index by [22]:

$$n_2 = \Delta\Phi_\circ \lambda / 2\pi I \, L_{eff} \tag{15}$$

Where $S = 1 - \exp(-2r_a^2/\omega_a^2)$ is the linear transmittance of the aperture(S=0.41), r_a the aperture radius and ω_a the radius of the beam at the aperture. I is the intensity of the laser beam at focus z=0, $L_{eff} = (1 - e^{-\alpha\ell})/\alpha$ is the effective thickness of the sample (ℓ is the sample thickness) , α is the linear absorption coefficient of the sample and $k = 2\pi/\lambda$ is the wave number.

The normalized transmittance of pure nonlinear refraction is given by [24]:

$$T(z) = 1 + \frac{4x\Delta\Phi_\circ}{(x^2+9)(x^2+1)} \tag{16}$$

where $x = z/z_\circ$, $z_\circ = \pi\omega_\circ^2/\lambda$ is the diffraction length of the laser beam, and $\omega_\circ$ is the laser beam waist at the focal point.

From Eqs. (14) and (15), the nonlinear refractive index n_2 can be obtained and the corresponding changes in the refractive index $\Delta n = n_2 I$ can be obtained too. The theoretical fit results showed that the peak to valley ΔT_{P-V} indicates the negative sign of nonlinear refractive index, n_2, (self-defocusing) for azo dye solution. Closed aperture data shows that the peak-valley normalized transmittance $\Delta T = 0.73$.

The nonlinear absorption coefficient β can be estimated from the open aperture Z-scan data using the relation [22]:

$$T(z,s,1) = \sum_{m=0}^{\infty} \frac{[-q_\circ(z)]^m}{(m+1)^{3/2}} \qquad \text{For } |q_\circ(0)| < 1 \tag{17}$$

where $q_\circ(z) = \beta I L_{eff} / (1 + (z^2/z_\circ^2))$

The expression of the on-axis total refractive index change, Δn, can be written as [25] :

$$\Delta n = \frac{dn}{dT} \cdot \frac{I\alpha\omega_\circ^2}{4k} \tag{18}$$

where dn/dT is the thermo-optic coefficient, and k is the ethanol thermal conductivity (k=0.0193 W m^{-1} K^{-1}).

With the help of equation (14,15,18), the thermo-optics coefficient, dn/dT, the total change of refractive index , Δn, and the nonlinear refractive index , n_2, are calculated. The results are given in Table 3.

Table 3.The measurement details and nonlinear optical parameters.

Laser beam wavelength (λ)	532 nm
Lens focal length (f)	+50 mm
Incident intensity at the focus (Z=0)	5.44 kWatt/cm^2
Effective sample thickness (L_{eff})	0.089mm
Nonlinear refractive index (n_2)	- 3.58x10^{-8} cm^2/W
Nonlinear absorption coefficient (β)	6.978x10^{-4} cm/W
The change in the refractive index (Δn)	- 1.951x10^{-4}
Thermo-optic coefficient (dn/dT)	0.257 10^{-5} k^{-1}

5. Conclusion

The electrical and optical properties of azo dye (4-Acetaminophenol – [2-(4-Azo)]-4-Aminodipheyl sulfone) have been investigated. The dielectric constant ε' and dielectric loss ε''

depend on the frequency between (50-500) KHz and are nearly constant beyond. The calculated values, at room temperature, of optical dielectric constant ε_L is 2.7 and the high-frequency dielectric constant $\varepsilon_\infty = n_\infty^2$ is 2.56 based on optical properties. The estimated values of E_0 and E_d are 3.59 eV and 16.35 eV, respectively. The energy band gap of this component is determined by the reflection spectra. The optical band is estimated to be 3.43 eV. The values of M_{-1} and M_{-3} are high, which indicates that the studied samples have high polarization. According to Millers rule, the value of non-linear optical susceptibility $\chi^{(3)}$ is 4.03×10^{-14} esu.

An investigation of the nonlinear properties of the azo dye in the ethanol solution by the Z-scan technique has allowed the evaluation of the values of the nonlinear refractive index and the nonlinear absorption coefficient. Thus, a (4-Acetaminophenol – [2-(4-Azo)]-4-Amino dipheyl sulfone**)** with many attractive linear and nonlinear optical properties is a suitable candidate for optoelectronic applications.

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