Study Of Solvent Effect On Uv-Visible Spectra Of A Newly Synthesized Azo-Dye, 2-(3-Carboxyl-4-Hydroxylphenyl)-1-(4-Nitrophenyl) Diazene (PNA-SA)

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ABSTRACT: The study of solvent effect used to describe the pronounced charge in position of Uv-visible absorption band that accompanies change in the polarity of the medium. Para nitro aniline-salicylic acid (PNA-SA)is newly synthesized compound which has different position of Uv-visibile absorption band in the protic and nonprotic solvents. The study was aimed to study the solvatochromism, band appointment charge transfer, dipole moment. The wavelength and intensity absorption bands are both affected when a molecule is solvent environment. This is due to unequal perturbation of the ground state and exited state. The basic parameters of each individual band were proportional to the energy and the probability of corresponding transition. The absorption spectra Para nitro aniline-salicylic acid (PNA-SA) was found to be two main bands at which350nm which saw that hypsochromic/ shift with n →π* transition and 375nm shows bathochromic shift with π →π* transition which result high dipole moment difference between the ground state (8.2107D) and exited state(35.8877D) with the moderately efficient charectestic of charge transfer with 59% . Thus, it is possible to conclude that PNA-SA can be used as a good solvent polarity probe.

Keywords: Paranitroaniline-salicylicacid, Solvatochromism, Band, Uv-visible Absorption, Charge transfer.

1. INTRODUCTION

Para nitro aniline-salicylic acid is an azo compound that characterized by the group-N=N- combined with one hydrocarbon radical. The most important diazo-compounds are those formed by the reaction of primary aromatic amines in acid medium with nitrous acid, by a reaction called Diazotization. Diazonium compounds are relatively unstable, very reactive compounds.Thier stability is greater at low temperature and in the presence of excess mineral acids. Therefore, most diazonium salts are produced at 0-10^0C in strong acid [1], [2].

1.1. Solvent effects

The wave length and intensity of absorption bands are both affected when a molecule is in solvent environment. This is due to unequal perturbation of the ground and exited electronic state of molecule which depends on the nature of the solute-solvent interactions [3],[4],[5]. The interpretation of solvent effect is often made difficult, because they are small and not easy to measure precisely and also because several individual effects, superimposed on one another, contribute to the observed changes[5].The dipole moment difference between exited state and ground state indicates the solvent effect on solvatochromic shift. The ground state dipole moment μ_g was calculated using a method of Gaussian soft ware. The exited state of dipole moment μ_e was determined by Lippert-mataga method, which is based on the measurement of the absorption spectrum shift with respect solvent polarity function Δf [6].

$$\Delta f = f(\varepsilon) - (0.5)f(n^2) = \frac{\varepsilon}{2\varepsilon+1} - \frac{1}{2} \frac{n^2}{2n^2+1} \quad (1)$$

Where; ε is dielectric constant, n refractive index, The Lippert-mataga equation has form:

$$\Delta v_{ss} = v_a - v_f = \frac{2}{hc}(\mu_e - \mu_g)^2 a^{-3} \Delta f + constant \quad (2)$$

Where: h, Planck's constant, a, on sager radius V_{sol} & v_0, observation maxima wave numbers Solvent effect on absorption spectra has both qualitative and quantitative .Quantitatively, the spectra shifts to the refractive index while the qualitative and comprehensive treatment of solvent effect have been sought to interpret spectra shift in terms of combination of dipole polarization of solute molecule and hydrogen bonding effect [5].

1.2. Electronic spectra

In unsaturated system , pi-electrons predominantly determine the state of electron sheath which are exited by the absorption of uv/vis-light. There are unshared electrons in molecules like nitrogen , oxygen , et.c are usually called n-electrons. Non-bonding electrons are bound less strongly than the bonding electrons Typical electronic spectra in organic compounds are π→π* and n→π* transitions. The π→π* transition is very intense (allowed) or weak (forbidden). But, the n→π*transition is generally forbidden and weak intensity. Azo compounds exhibits n→π* transition characteristic of the N=N group, the intensity of the band depends on stereochemistry of nitrogen-nitrogen linkage of straight chain compounds containing nitrogen-nitrogen bond give rise to low intensity band in the near Uv-visible-region[2],[4]. The solvent effect on spectra, resulting from electronic transitions, is primarily dependent on the chromophore and the nature of transition (∂→∂*, n→∂*, n→π*, π→π) and charge transfer (CT) absorption. The electronic transitions of particular interest in this respect are n→π*, π→π, transfer (CT) absorptions [6].[7]. Organic molecules composed of directly attached electron donor and electron acceptor moieties have received considerable attention as possible models for a number of photochemical and photo biological processes. Excitation of such molecules induces transfer of an electron

from donor to acceptor and is often accompanied by rotational relaxation to a twisted conformation of the donor relative to the acceptor, forming the so-called Twisted Intramolecular Charge Transfer (TICT) state [8], [9]. Molecules of the type D- π -A where the donor and acceptor groups are connected to the ends of a conjugated system exhibit large changes in dipole moment ($\Delta\mu$) up on excitation due to photo induced Intramolecular charge transfer process. The extent of charge transfer depends on the nature of the donor (D) and acceptor (A) groups and the length of the π system. Conformational dynamics of the D and A fragments can also significantly influence the photochemistry of such systems. The π^* scale is based on solvent induced shift of the longest wave length $\pi\rightarrow\pi^*$ absorption band is indicator of the type D- π -A [10]. The relevance of this paper on PNA-SA which is newly synthesis through diazotization is, greatly studied its characterization of solvent effect ,Solvatochromism shift ,and electronic spectra in the Uv/vis-spectroscopy.The study was also aimed the characterization of PNA-SA at investigating the effect of various solvents ;in relation to study solvatochromism ,electronic spectra ,and band appointment. In addition to this, the effect of dielectric constant and refractive index is also studied. The solvents chosen for study were water, dichloromethane, chloroform, ethanol, acetonitrile, diethyl ether, carbon tetrachloride, Isopropanol, n-hexane, methanol, dichloromethane e.t.c.

2. EXPERIMENTAL SECTION

Apparatus: Beaker, Pasture pipettes, Suction filtration set up, Test tube, Glass rod, Erlenmeyer flask, Digital melting point apparatus (SMP10).

Chemicals: Paranitroaniline, Conc.HCl (purchased from BDH chemicals), Salicylic acid (purchased from Aldrich chemicals), 22% of NaOH solution.

2.1. Synthesized of 2-(3-Carboxyl-4-Hydroxylphenyl)-1-(4-Nitrophenyl)Diazene

Preparation of solution A (diazotization of Para nitro aniline, PNA):1.5g PNA was placed in 100ml of beaker, 40ml of water and 2.5ml conc.HCl was added .stir and the solution of the in beaker was warmed over wire gauze until a clear solution was resulted. The sample was placed in ice bath and cooled to 0-5^{0}c the crystalline form of PNA-hydrochloride was separated into tiny divided crystalline form.1.5g of NaNO$_2$ in 8ml water was added slowly and being stir with a temperature of 0-5^{0}C. Finally, the diazonium salt solution A, was kept in ice bath (about 45minutes) until it was resulted clear solution.

Preparation of solution B: 1.5g of salicylic acid was prepared in 50 ml of Erlenmeyer flask with 8ml of 22% NaOH solution and finally was added 10ml of water. At the end, to get complete synthesized PNA-SA, solution B was

added into solution A. then stir and HCl was added drop by drop. The mixed solution was kept at room temperature in order to form crystal of PNA-SA. After crystal was formed, it was recrystalized using suction filtration, and it was also checked its purification using melting point method and thin layer chromatography (TLC) The absorption spectrum was measured linearly in wave numbers in SP-65 UV/Visible spectrophotometer using a 1cm thickness quartz cuvate. The solvents were supplied by BDH chemicals Ltd pool England. These are: Methanol, Ethanol, Isopropanol, chloroform, Carbontetrachloride, Diethyl ether, Dichloromethane, Ethyl acetate, n-hexane, Acetonitrile, Water, n-butyl alcohol
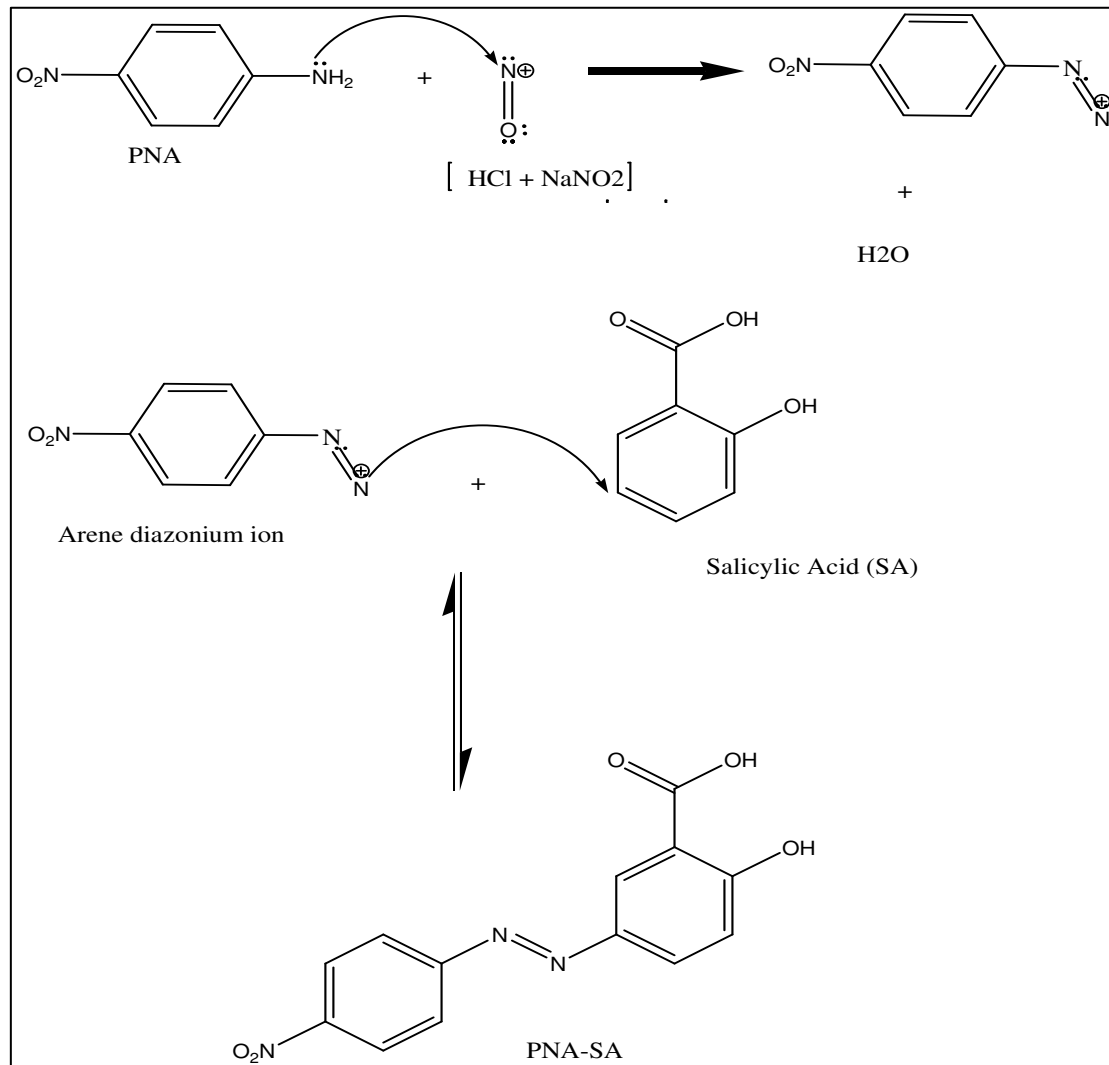
Fig.1. *Reaction Mechanism for Synthesis of PNA-SA*

2.2.   Computational Details

The minimum ground state structure of PNA-SA was obtained by optimizing the ground sate geometry at DFT level with B3LYP functional and 6-31G basis set using Gaussian 03 package.

3.   RESULT AND DISCUTION

3.1. Purity determination

The purity of sample PNA-SA has been checked through melting point determination and thin layer chromatography (TLC). The melting point of PNA-SA did not show deviation from previously measured that is 160 ^{0}c and also tested the purity by placing a drop of sample in stationary phase of thin layer chromatography, the drop did not separated into multiple spots i.e. a single spot was only clearly shown. Therefore, the result obtained from both method shows that the newly synthesizes PNA-SA is high pure diazo compound.

Absorption spectra

The absorption spectra of PNA-SA in solvents of different polarities were measured with the aim of probing the effects of solvent polarities on the electronic absorption spectra of the compound. A series of absorption spectra of PNA-SA were recorded in n-hexane, chloroform, dichloroethane, ethyl acetate, diethyl ether and acetonitrile solutions in order to study the role of solvent polarity in modifying the electronic states of the compound (Fig.1). More elaborated data is presented in table1.
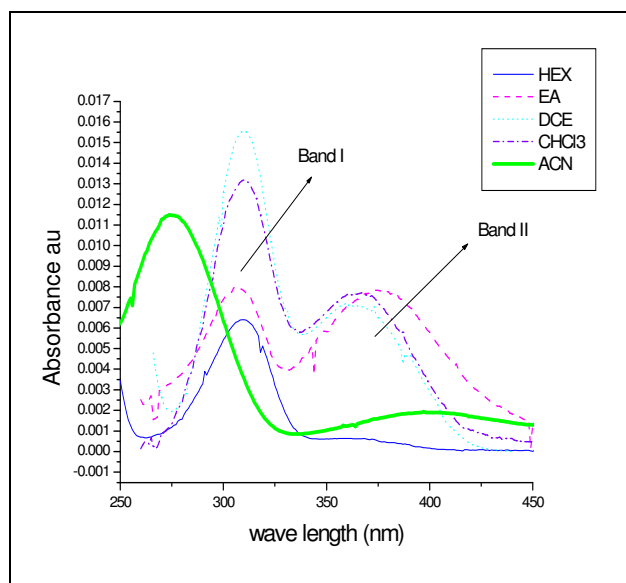
Fig.2. *Area Normalized Absorption Spectra of PNA-SA in NonProtic Solvents of Different Polarities.*

The basic parameters of each individual band-band- I and II were proportional to the energy and the probability of the corresponding transitions. At the same time, the maximal intensity or the area of band was proportional to concentration of the absorbing particle. This fact gives chance for qualitative analysis after resolution of the overlapping bands had been performed. Quantitative interpretation of these results, must take into account that the integrated intensity or the area of each individual band presented in absorption units, is proportional to the concentration of observing PNA-SA. Hence, the area of sub band can be related with concentration of each PNA-SA form [11], [12].

TABLE 1.
Shows That Dielectric Constant And Refractive Index Of Selected Solvents.

solvent	ε	N	Δf	ET	Band I(nm)	Band II(nm)
n-hexane	1.890	1.3749	0.0931		309	-
Chloroform	4.89	1.4459	0.25561	0.259	310	367
Dichloroethane	10.36	1.4448	0.32587	0.327	310	360
Diethyl ether	4.2	1.3524	0.25144	0.117	307	359
Acetonitrile	35.94	1.3441	0.39199	0.46	274	397
Ethyl acetate	6.02	1.3724	0.29230	-	306	374
Methanol	32.66	1.3284	0.39297	0.762	288	379
Ethanol	24.55	1.3614	0.3794	0.654	305	360
2-propanol	82.2	1.3772	0.3974	0.546	299	389

Two main absorption bands in nonpolar protic solvents and a single absorption band in the non-polar solvent n-hexane characterize the absorption spectra of the compound. The first band around 305 nm is found to show a hypsochromic shift (310nm for chloroform and 274 nm in Acetonitrile giving Δλ= -36 nm) showing that the band is more of an n→π* transition of the -N=N- group. Such a shift is clearly shown in the peak-normalized spectra of band I in fig.3.and plot of wavelength maxima of band I versus Solvent polarity parameter Δf.
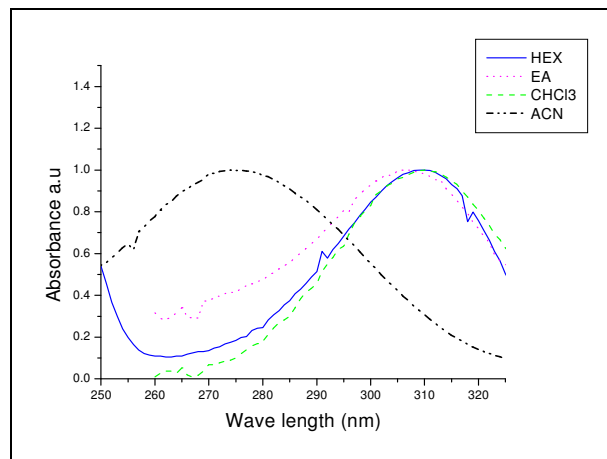

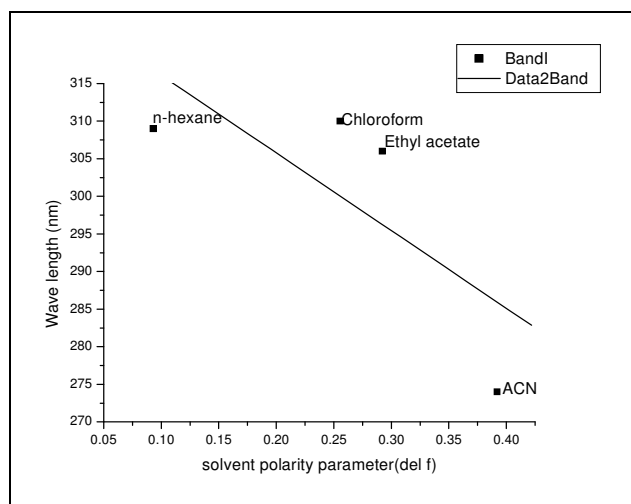**Fig.3.** *Area Normalized Absorption Spectra of Band I in Selected Solvents.*

Fig.4. *Plot of Absorption Wavelength Maxima of Band I versus Solvent Polarity Parameter (∆f)*

A plot of absorption wavelength maxima of band I versus solvent polarity parameter in non-hydrogen bonding solvent (n-hexane, chloroform, ethaylacetate, acetonirie) we have shown that with increasing both dielectric and refractive index, as you going from n-hexane to acetonitrile solvent polarity is increases. The result toll the spectra change was shifted to lower wavelength. This is due the reason that ,less polar interaction of solvent (n-hexane, chloroform, ethylacetatae, acetonitrile) with PNA-SA in terms of the dipole- dipole   interaction , there by resulting   in net stabilization of the ground state molecule and hence it shows   hypsochromic   shift in the spectrum[12],[13]. Phenomena that were more interesting observed in band II located around 375 nm. The band is found to be highly dependent on solvent polarity and it shows a bathochromic shift with increasing solvent polarity. A shift of $\Delta\lambda$= 39 nm is obtained for the band (i.e. 358 nm in n-hexane and 397 nm in Acetonitrile) showing that the band is a $\pi\rightarrow\pi^*$ transition with large charge transfer character (CT spectra) and hence the possibility of photo induced intramolecular charge transfer with in the molecule. The Bathochromic shift of the CT spectra is indicated more clearly in Fig.5.
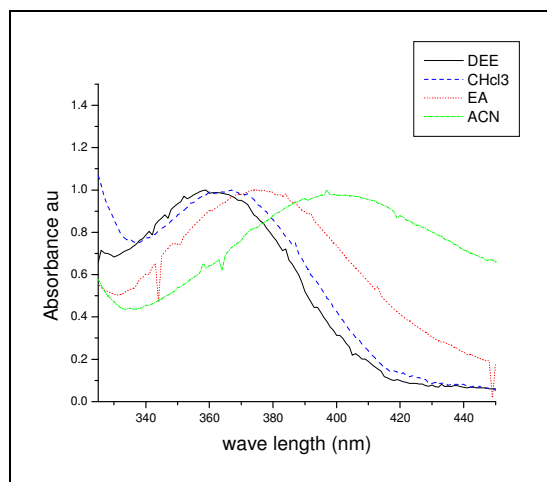

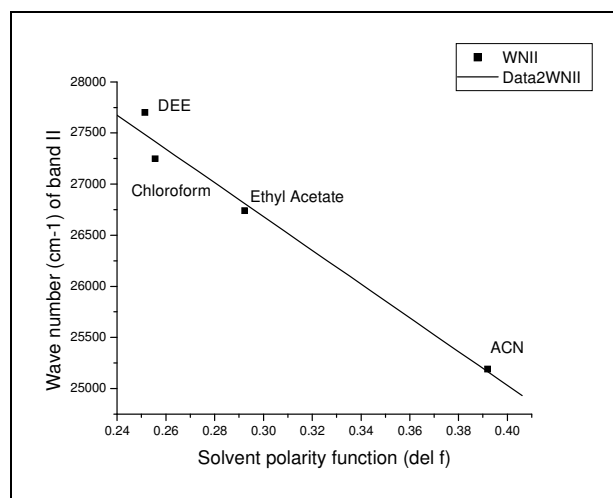**Fig.5.** *Charge Transfer Spectra (Band II) Of PNA-SA in Some Non-Protic Solvents of Different Polarities.*

Fig.6. *Plot of Absorption Wave Number (cm^{-1}) Of Band II versus Solvent Polarity Function (∆F)*

3.2.   Computational result
The ground state structure of PNA-SA was optimized by using Gaussian 03 package at DFT level with B3LYP functional and 6-31G basis set. The ground state dipole moment (μ_g) is found to be 8.2105 D
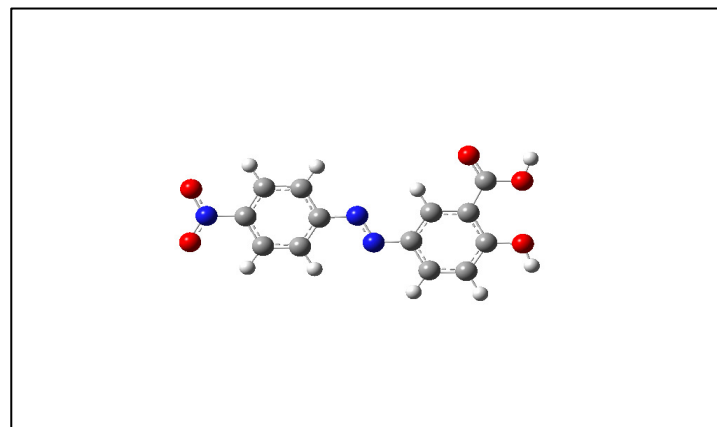

Fig.7. *Ground State Optimized Structure Of PNA-SA (At DFT Level B3LYP Functional And 6-31G Basis Set).*

3.3.   Excited state dipole moment
The ground state dipole moment was estimated 8.2107 D from   computational   result.The result of the regression analysis and lippert mataga equation , the of dipole moment change $\left(\mu_E - \mu_G\right)$ is found to be 27.677D. Hence the value of excited state of dipole moment (μ_E)found to be 35.8877 D. in this analysis the molecular radius, *a* was 3.85 A^0 ,using Gaussian 03 package and hyperchemsoft 1.5 ware from optimized molecular structure. The spectra on the band-II is highly with an intermolecular charge transfer(CT) absorption can exhibits a bathochromic shift. Hence, the charge transition (CT) involves ground (8.2107D) and exited states (35.8877D) with deferent dipole moment. This suggests that the CT absorption band should exhibit marked solvent polarity effect. The electronic transition ($\pi\rightarrow\pi^*$) is intramolecular charge transfer from the electron-donor OH-group part to acceptor part NO_2-group.

3.4.   Charge transfer efficiency

The distance r, 12.47895 A^0 between charge transfer species ($D-\pi-A$) was estimated using Gaussian 03 package and hyperchem soft 1.5 ware from optimized molecular structure and ideal dipole moment was obtained 59.99D. The excremental dipole moment at the excited state was found to be 35.8877D. According to the given formula Charge transfer efficiency of PNA-SA is 59% which tell us, moderately charge transfer is happen between $D-\pi-A$ (OH-group and NO_2-group)[14]. Ideal dipole moment for a complete charge transfer

$$\mu_e = er \qquad (3)$$

Where e is the charge of an electron and r is the distance between charge transfer species. The real charge transfer during light absorption is determined from the solvatochromic data, which is the μ_e experimental. An increase the exited state dipole moment with respect to that of the ground state corresponds to positive solvatochromism (bathochrtomism band shift upon the increase of solvent polarity [6]. Rough estimation of the transfer efficiency:

$$Charge\ transfer\ efficieny = \frac{\mu_e ideal}{\mu_e experimental} x\ 100\% \qquad (4)$$

4.   CONCLUSION

The absorption spectra of PNA-SA is found to be highly depends on polarity of solvents. It has two main absorption bands at 305nm, which shows a hypsochromic shift with n→π* transition character, characteristics of -N=N- azo-linkage and   at   375nm, highly dependant on solvent polarity that indicate   a bathochromic shift with π→π* transition with large charge transfer character involving the whole molecule. In general, the molecule is characterized spectroscopically by low intensity n→π* band and a high intensity π→π* band in the UV region. Increase the charge transfer character(CT)of the transition π→π* along the long molecular axis and shifts the corresponding band for the red, thus overlapping the weak   n→π*   band. The CT character of the band causes strong dependence of the band position on solvent polarity. In addition to this, high dipole moment difference between ground states and excited state shows characteristics of charge transfer (CT). The dipole moment of the molecule in the ground state is different from that of the excited state. If the dipole moment of the molecule in the ground state is greater than that of the excited state, polar solvents stabilize the molecule in the ground state than they do in the excited state and thereby the energy of the molecule in the ground state is lowered more than its energy in the excited state, and the energy gap is increased. As a result the absorption band shifts to lower wavelength region, hypsochromic (or blue) shift and Vic versa.   From the results so far, the ground state dipole moment, computed at DFT level and B3LYP functional and 6-31 G basis set, is found to be 8.2107 D and the excited state dipole moment, μ_e is found to be 35.8877 D showing a large dipole moment change consistent with the spectral behavior. The ideal dipole moment is calculated to be **59.99D.** Therefore, the charge

transfer efficiency becomes 59%. Thus, it is possible to conclude that PNA-SA can be used as a good solvent polarity probe.

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