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Perturbation of absorption spectra properties of 4, 5-Dimethyl-2-nitro aniline by polar, non polar solvents and substituents

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ABSTRACT

The UV-absorption spectra of substituted aniline have been recorded in the UV/visible region in three solvents of different polarity. The effect of solvent polarity on the position and intensity of the absorption bands has been demonstrated. The variations in $\pi \rightarrow \pi^*$ transitions corresponding to the main absorption bands of benzene are discussed. The influence of substituent on the absorption spectra is also discussed in this paper.

Keywords: 4, 5-Dimethyl-2-Nitro Aniline, Absorption-bands, solvent effect, substituent effect.

INTRODUCTION

Electronic spectroscopy is concerned with electron transition between orbital of different energy, usually from the occupied orbital of highest energy to vacant orbital of lowest energy. The excitation is as a result of absorption of light, the quantum energy (E) of which is a function of frequency (v). However not all absorption of radiation by organic molecules result in electronic excitation, the probability of excitation depends on the wave functions of both the ground and excited states of orbital concerned. The rules about which a transition is allowed or forbidden, is a functions of symmetry and multiplicity of the ground and excited state of the orbital concerned. The electronics excitation in a molecule is accompanied by change in vibrational and rotational quantum numbers; therefore what supposes to be absorption lines becomes a broad peak containing vibrational and rotational fine structures. However, the interaction of solute and solvent molecules blurred out the fine structures and a smooth curve is observed. [1], [4], [6], [26]

Aniline and its substituents posses a wide ranging potential for application in pharmaceutical, herbicides and dye industries. Due to the wide usefulness of derivatives of anilines, several investigations have been carried out in order to understand the characteristics of electronic states of these molecules. However, theoretical consideration of the electronic properties of these systems are lacking as very few theoretical studies have been carried out on their electronic spectroscopy. The understanding of their structure, molecular properties as well as nature of reaction mechanism they undergo has great importance and has been the subject of many experimental and theoretical studies. Therefore, as part of our investigations on spectroscopy, we carried out the detailed experimental studies on the electronic absorption spectra. Literature survey reveals that no electronic spectral study on 4, 5-Dimethyl-2-Nitro Aniline has been carried so far. The aim of present investigation is to study the effect of solvents and substituents on the absorption spectra of 4, 5-Dimethyl-2-Nitro Aniline. The aim of present study is twofold namely:

i) To record the electronic absorption spectra for the substituted anilines in different solvents and to study the effect of these solvents on the absorption spectra.
ii) To study the effect of substituents on the absorption spectra.

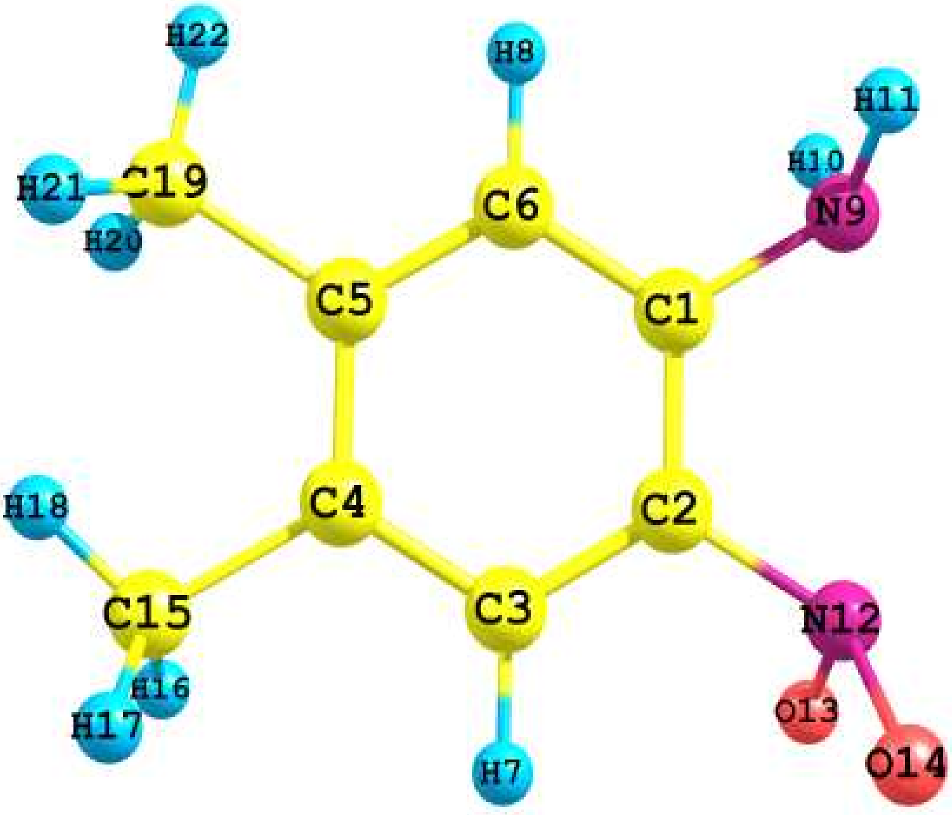

Figure 1: Molecular structure of 4, 5-Dimethyl-2-Nitro Aniline

MATERIALS AND METHODS

The compound 4, 5-Dimethyl-2-Nitro Aniline in the solid form was purchased from Sigma Aldrich Chemical Pvt. Ltd., Germany with a stated purity of greater than 99% and was used as such without further purification. UV/visible spectra of 4, 5-dimethyl-2-Nitro Aniline was recorded in three solvents of different polarity. The solvents were distilled several times to spectroquality grade, while the solute was used without further purification.

RESULTS AND DISCUSSION

Electronic absorption spectrum of 4, 5-Dimethyl-2-Nitro Aniline molecule is expressed with respect to electronic transition bands of benzene molecule. The simplest aromatic compound to consider is benzene. Aromatic compounds have relatively complex absorption spectra with several bands in the ultraviolet region. We have discussed these bands using Braude's E and B notation [6]. B band is generally found between (230-280) nm. Three different $\pi \rightarrow \pi^*$ transitions are found in benzene (and related compounds), i.e., two E bands [E_1 = 184 nm, E_2 = 204 nm] and a B band (Benzenoid) at 256 nm. The intense band near 180 nm results from an allowed transitions, whereas the weaker band near 200 and 260 nm results from forbidden transition in the highly symmetric benzene molecule. In the absorption spectra of aniline two absorption bands due to $\pi \rightarrow \pi^*$ transition are observed at 230 and 280 nm. Absorption bands of benzene and aniline are summarized in Table1.

The absorption spectra of 4, 5-Dimethyl-2-nitro Aniline mainly consist of two sharp absorption bands in the specific electronic transition spectral range and these two bands are identified as $\pi \rightarrow \pi^*$ transition bands [2]-[5]. However, these absorption bands exhibit different behaviors according to the nature of the substituents on the basic aromatic benzene ring and the type of solvents used. Electronic absorption spectra of the present molecule is observed in three different solvents namely; carbon tetrachloride, diethyl ether and propane-2-ol. First absorption band which is highly intense observed in the region from (250-350 nm) in these three solvents [7]-[10]. This band is originated due to $\pi \rightarrow \pi^*$ transition and is known as E_2 band. Bands observed at 282, 282, 289 nm in carbon tetrachloride, diethyl ether and propane-2-ol are designated as E_2 band. These bands are in close agreement with the results of earlier researchers.

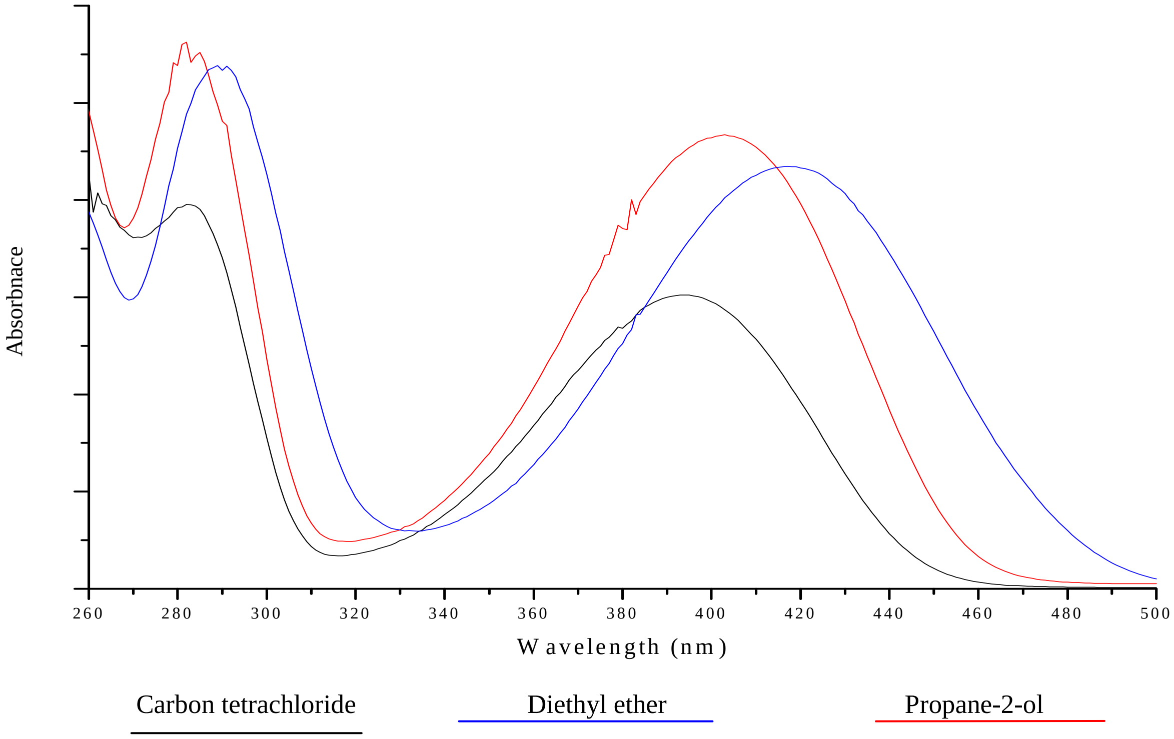

Figure 2: Electronic absorption spectra of 4, 5-Dimethyl-2-Nitro Aniline in carbon tetrachloride, diethyl ether and propane-2-ol.

Second broad and sharp absorption band lies in the range from (350-500 nm). This band is designated as B-band. In the present investigation absorption bands at 394, 403, 413 nm in carbon tetrachloride, diethyl ether and propane-2-ol respectively are originated from π→π* transition. The electronic absorption spectra of this aniline consist of two absorption bands none of which correspond to n→π* transition band. This is supported by the high intensity of the absorption bands. Also, the absorption bands corresponding to n→π* transitions are blue-shifted and blurred in polar solvent. The observed bands in the Figure 2 correspond to π→π* transitions and the expected n→π* transition is submerged under the strong π→π* transition one. Position of electronic transition bands are totally dependent upon the type of solvents used to record as well as the substituents on the benzene ring [11]-[13]. Now we will discuss these effects one by one in section 3.1 and 3.2.

3.1 Effect of substituent on the absorption spectra

Substituent has an effect on absorption maxima. An alkyl group, for example, causes only a small shift by about 5 nm, whereas an additional conjugated C=C double bond moves the absorption maximum 30 nm to higher wavelengths. We call this a "red shift". The opposite would be a "blue shift", when the absorption peak moves towards smaller wavelengths. Benzene, for example, has its highest absorption wavelength at 254 nm. A benzene with an amino substituent absorbs only a little higher, at 280 nm. However, there are some combinations of substituents which give rise to an unusually large "red shift". This is the case when an electron-donating and an electron-withdrawing substituent are placed in para position to each other on a benzene ring. So, while the amino group in 4-nitroaniline donates electron density to the benzene ring, the nitro group at the other end withdraws it which gives rise to an additional resonance structure [14]-[15]. Such a push-pull arrangement between an electron-donating and an electron-withdrawing group results in a considerable red shift. "Push-pull" systems are a common feature of many dyes.

TABLE 1 Electronic absorption bands of Benzene and Aniline molecule

Molecule	E_1-band (nm)	E_2-band (nm)	B-band (nm)
	π→π*	π→π*	π→π*
Benzene	184	204	256
Aniline	-	230	280

The electron donating methyl group interacts with nearby systems through hyper conjugation, while the NH_2 shares its lone pair electrons with the ring. Both the effects imply electronic delocalization and are taken into account by the molecular orbital approach. An auxochromic group like NH_2 and CH_3 substituted to chromophore shifts both the E_2 and B band towards the longer wavelength with the intensification of B-band and loss of its fine structure as shown in the Table 2. This loss of fine structure is mainly due to n→π* transition. As mentioned in the earlier researchers [16]-[18] that amino group has non bonding electrons and they will participate in n→π* transition. This perturbation effect in the absorption spectra due to the presence of these auxochromes depends on the extent of interaction between the substituent and the π-system of the benzene nucleus.

With some minor exceptions amino groups are strong electron donors. In auxochrome substitution, the hetroatom with loan pair of electrons shares these electrons with the π electron system of the ring facilitating the π→π* transition and thus causing a red shift of E_2 band. The occurance of E_2 band above 210 nm is due to the shift of π→π* transition towards the longer wavelength, which is originated due to combined mesomeric, inductive, hyperconjugation and steric effects exerted by auxochrome and alkyl substitution on the aromatic ring.

Effect of amino group on the electronic absorption spectra is of great interest because of its positive mesomeric effect. Due to positive mesomeric effect the parent amino group is a strong electron donor. For amino groups the extent of conjugation with aromatic ring reflects the facility of nitrogen to assume the sp^2 hybridization. Thus donor strength of amino group depends mainly on its resonance interaction with aromatic ring. For the molecule in the present investigation, a strong electron withdrawing NO_2 group is placed at the 2^{nd} position. If any of simple chromophore is conjugated with other, a multiple chromophore is formed having a new absorption band which is more intense and at a longer wavelength than the strong bands of simple chromophore. So due to the presence of this NO_2 group there is a strong bathochromic shift in the absorption bands of the reference benzene absorption bands. The E_2 band which is originated due to $\pi \rightarrow \pi^*$ transition is shifted to longer wavelengths 282, 282, 289 nm in carbon tetrachloride, diethyl ether and propane-2-ol respectively from its original position of 204 nm in benzene molecule. So this red shift towards the longer wavelength is mainly affected by the presence of this nitro group.

B-band is also shifted to a very high wavelength of 394, 403 and 413 from the original position of 254 nm of the reference benzene molecule. Such a higher shift is again due to this electron withdrawing nitro group at the 2^{nd} position. As mentioned earlier the alkyl substituent contribute very less in the red shift of these $\pi \rightarrow \pi^*$ transitions. This result agrees very well with the earlier researchers [19]-[23].

Steric hindrance also affects the influence of an auxochrome on a chromophore. Electron systems conjugate best when the molecule is planar in structure. If the presence of an auxochrome prevents the molecule from being planar, then large effect is noticed in the absorption spectra. Due to this reason -meta and -para substituted methyl groups in the present molecule have predictable but slight effect on the absorption spectra. Whereas the NO_2 group at -ortho position alter the spectrum completely. The observed bands in Figure 2 correspond to the $\pi \rightarrow \pi^*$ transition and the expected $n \rightarrow \pi^*$ transition is submerged under strong $\pi \rightarrow \pi^*$ transition one. This result is in close agreement with the earlier researchers [24]-[25].

3.2 Effect of solvents on the absorption spectra

To study the effect of solvents on the absorption spectra three different solvents are used here. Absorption spectra are mainly affected by the polarity of the solvent [3], [4]. So taking into consideration this point the absorption spectra in the present investigation is studied in two non polar solvents (carbon tetrachloride, diethyl ether) and a polar solvent (propane-2-ol). Specific properties (dielectric constant, refractive index, dipole moment) of these three solvents are mentioned in Table 2.

TABLE 2: Effect of solvents on electronic transition of 4, 5-dimethyl-2-nitro aniline

Solvent	Dielectric Constant	Refractive index	Dipole moment	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
				E_2-band	B-band
CCl4	2.24	1.461	0	282	394
DEE	4.33	1.352	1.30	282	403
Propane-2-ol	18.3	1.377	1.66	289	413

The effect on the absorption spectrum of a compound when diluted in a solvent will vary depending on the chemical structures involved. Generally speaking, non-polar solvents and non-polar molecules show least effect. However, polar molecules exhibit quite dramatic differences when interacted with a polar solvent. Interaction between solute and solvent leads to absorption band broadening and a consequent reduction in structural resolution and intensity of absorption maxima. In the present investigation similar type of behavior is shown by the E_2 band in both the solvents in spite of different polarities of carbon tetrachloride and diethyl ether. In both the solvents E_2 band, due to π→π* transition is observed at 282 nm; however the intensity of absorption maxima in diethyl ether is higher. It means a hyperchromic shift on moving from carbon tetrachloride to diethyl ether [26].

More polar solvents tend to negate the fine structure due to the effect of solvent broadening. These solvent broadening effects are a result of environmental heterogeneity arising from the collisions and interactions of solvent molecules which leads to the addition of hundreds of vibration and rotational energy states which subdivide the less numerous electronic levels. The addition of these many of hundreds of absorption bands, all closely spaced together, leads to a broad spectral envelope. The level of this broadening will depend strongly on the polarity of the solvent. Polar solvents are more likely to involve weak hydrogen bond interactions which are roughly of the order of rotational and vibrational energies. Consequently, the effect of a polar solvent is to introduce even more overlapping or closely spaced absorption bands which lead to further line broadening or loss of resolution [4], [6], [18]. With increase in solvent polarity, the maximum spectroscopic absorption bands of 4, 5-Dimethyl-2-nitro aniline experience a red shift (bathochromic shift) indicating a positive solvatochromism. These facts can be explained in terms of the greater stabilization of the charge separated excited state compared to the ground state by greater solvating power of polar solvents through specific (hydrogen bonding) and nonspecific (dipole-dipole) interaction, which reduces the energy difference between ground and excited state and hence reducing the maximum energy of absorption. Nitro group is solvated by hydrogen bonding interaction (i.e. hydrogen bond donation from solvent to solute). Conversely amino group is solvated by hydrogen bonding interaction (i.e. hydrogen bond donation from solute to solvent) [1], [4], [26]. So while moving from a non polar carbon tetrachloride to propane-2-ol, E_2 band observed to exhibit bathochromic shift from 282 nm to 289 nm. Similar type of behavior is also shown by the second π→π* transition/B-band. Absorption band of 394 nm in carbon tetrachloride is shifted to a longer wavelength of 413 nm in propane-2-ol with the increased intensity of the absorption maxima (i.e. hyperchromic shift). So both the π→π* transitions show a bathochromic shift and hyperchromic shift with increase polarity of the solvent in the titled compound. This type of bathochromic shift and hyperchromic shift with increased intensity is observed by several researchers [12]-[16].

CONCLUSION

In the electronic absorption spectra of 4, 5-Dimethyl-2-Nitro Aniline two absorption bands are observed: the E_2 band due to π→π* transition and B-band also due π→π* transition. These transitions are strongly dependent on both, the nature of the substituent as well as the solvent in which the spectrum is recorded. π→π* transition shows a bathochromic shift while going from non-polar to polar solvent. In addition to this n→π* transition is absent for the present molecule.

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