



The electronic absorption spectra of pyridine azides, solvent–solute interaction

Rafie H. Abu-Eittah^{a,*}, Mahmoud K. Khedr^b

^a Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

^b Department of Chemistry, Faculty of Science, Beni Suef, Egypt

ARTICLE INFO

Article history:

Received 28 November 2007

Received in revised form 28 May 2008

Accepted 23 June 2008

Keywords:

Pyridine azides

Absorption spectra of pyridine azides

Solvent–solute interaction and spectra of pyridine azides

ABSTRACT

The electronic absorption spectra of: 2-, 3-, and 4-azidopyridines have been investigated in a wide variety of polar and non-polar solvents. According to Onsager model, the studied spectra indicate that the orientation polarization of solvent dipoles affects the electronic spectrum much stronger than the induction polarization of solvent dipoles. The effect of solvent dipole moment predominates that of solvent refractive index in determining the values of band maxima of an electronic spectrum.

The spectra of azidopyridines differ basically from these of pyridine or mono-substituted pyridine. Results at hand indicate that the azide group perturbs the pyridine ring in the case of 3-azidopyridine much more than it does in the case of 2-azidopyridine. This result agrees with the predictions of the resonance theory.

Although the equilibrium = azide tetrazole is well known, yet the observed spectra prove that such an equilibrium does not exist at the studied conditions.

The spectra of the studied azidopyridines are characterized by the existence of overlapping transitions. Gaussian analysis is used to obtain nice, resolved spectra. All the observed bands correspond to $\pi \rightarrow \pi^*$ transitions, $n \rightarrow \pi^*$ may be overlapped with the stronger $\pi \rightarrow \pi^*$ ones.

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1. Introduction

The electronic absorption spectra of some aromatic azides have been studied in the visible–ultraviolet region using different solvents. The bands observed were assigned to intra-molecular charge transfer transitions and or locally excited ones, no evidence is given for $n \rightarrow \pi^*$ transitions [1].

Alky azides are characterized by two absorption bands, at 287 nm, $\epsilon = 25 \text{ mol}^{-1} \text{ L cm}^{-1}$ and at 216 nm, $\epsilon = 500$ [2]. Substitution by electronegative groups in the alkyl portion lowers, via induction, the energy of electrons on the nitrogen bonded to carbon and results in a blue shift of the two transitions [2], this effect was noted by Böhme [3,4] as well as by Lieber [5].

The general features of the ultraviolet spectra of aromatic azides have been investigated [6,7]. Generally, it can be said that the intensity of the long wavelength band ($\sim 285 \text{ nm}$) is substantially increased [8], data for aromatic and condensed aromatic azides indicate a red shift of the entire spectrum, with respect to that of alky azides, with increased intensity. The azide group is electron

donating with a Hammett constant $\sigma_p^+ = -0.54$ [6] and affects the spectrum of the aromatic ring itself in two ways: increases the size of the aromatic system and reduces the symmetry of the molecule [9].

The solution spectra of HN_3 have two bands, a weak band at 260 nm ($\epsilon = 40$) and a somewhat stronger band at 200 nm ($\epsilon = 500 \text{ mol}^{-1} \text{ L cm}^{-1}$), this spectrum has been interpreted by MO calculations. The spectra of alkyl azides have the same structure as that of HN_3 [2,5,8,10]. A weak band at 278 nm ($\epsilon = 25$) is assigned to the $\pi_y^n \rightarrow \pi_x^*$ transition and a stronger band at 216 nm ($\epsilon \sim 500$) is assigned to the $sp_z \rightarrow \pi^*$. The position and extinction coefficient of these bands are independent of the structure of the alkyl group and are remarkably insensitive to solvent changes [2].

Karvellas et al. [11] compared the calculated MNDO, AM1, PM3 ionization potential of 2-azidopyridine with photo electronic spectroscopy data and got the following results:

EXP	8.9	10.14	10.6	11.2	11.9
PM3	9.31	10.74	10.84	11.48	11.49
	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4

The difference in energy between HOMO-1 and HOMO-2 is less than 0.5 eV, which is a good evidence for the existence of three electronic transitions in the accessible UV spectrum of 2-azidopyridine.

* Corresponding author. Tel.: +20 2 35717623.

E-mail address: aboettah@yahoo.com (R.H. Abu-Eittah).

Experimental and theoretical studies of the photochemical properties of 4-azidopyridine and its derivatives have been reported [12]. The quantum yield of photodissociation of 4-azidopyridine (in acetonitrile) decreases from 0.8 to 0.2–0.3 upon protonation or methylation at the endocyclic nitrogen atom. Molecular orbital calculations for all the studied molecules confirmed the existence of a correlation between the type of orbital occupied in the excited state and the photochemical activity of the molecule.

The heterocyclic azides: 2-, 3-, and 4-azidopyridines are very effective surface modifiers upon photolysis forming films on a wide variety of surfaces. Applying the pyridine azide to the surface followed by photolysis generate highly active nitrenes which can react with many organic functional groups [13].

The neighbouring group affects significantly the properties of aryl azides [14]. It has been found that pyrolysis of 3-azido-2-nitropyridine leads quantitatively to the cyclic furazan 1-oxide.

In this work, the electronic absorption spectra of 2-, 3-, and 4-azidopyridines are investigated in a wide variety of solvents. Solvent–solute interaction and its effect on the spectra of the studied molecules is explored in terms of Onsager model.

2. Experimental

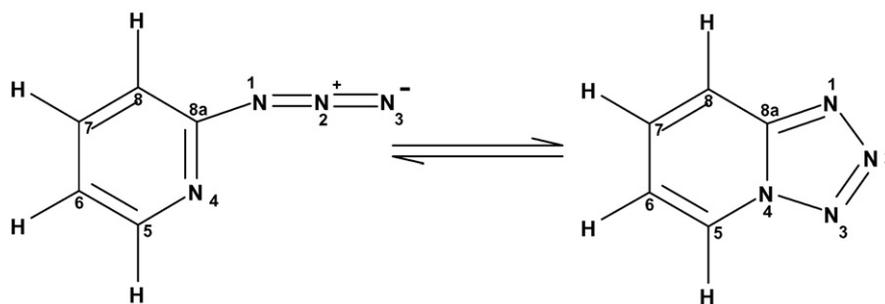
2.1. Solvents

Both polar and non-polar solvents are Merck-AR-grad reagents and were used without further purification.

2.2. Compounds

The studied compounds were prepared as cited in literature [15–17].

2-Azidopyridine was prepared by dissolving 2-aminopyridine or its hydrochloride in cold 10% hydrochloric acid, temperature (0–5 °C). Aqueous solution of sodium nitrite is added drop wise such that temperature does not rise above 5 °C. Aqueous solution of sodium azide is then added while the temperature is kept below 5 °C and stirring for 1 h. The solution is allowed to warm to room temperature, the obtained oil is extracted with methylene chloride. Evaporation of the dried extracts on a rotary evaporator (bath temperature below 50 °C) gave the crude azide.



3-Azidopyridine was prepared by dissolving 3-aminopyridine in concentrated HCl, and the solution was chilled to 3 °C in an ice bath [17]. NaNO₂ in ice-water was added drop wise during 25 min with stirring. A solution of sodium azide was added drop wise over a period of 30–40 min keeping the temperature at 0 °C. The reaction mixture was stirred for an additional time, 30–60, min at room temperature, then made alkaline with Na₂CO₃ and extracted with CH₂Cl₂. The extract was washed with water, dried over anhydrous MgSO₄ and evaporated in vacuum.

4-Azidopyridine was prepared by treating freshly prepared 4-chloropyridine with NaN₃ in dimethyl sulfoxide [16]. The purity of all the prepared compounds was confirmed by IR-spectral analysis where ν_{st} of the azide group appears at 2120–2140 cm⁻¹.

2.3. Apparatus

IR spectra were recorded on Jasco FT/IR Model 430. Ultraviolet and visible spectra were recorded using UV-1601 PC UV–vis (SHIMADZU) Spectrophotometer. Gaussian analysis of the observed spectra was performed using a Mathcad plus 6 package (from Mathsoft © 1986–1994 Mathsoft Inc.).

3. Results and discussion

3.1. 2-Azidopyridine

3.1.1. Electronic absorption spectra

Fig. 1 shows the electronic absorption spectrum of 2-azidopyridine in absolute ethanol as well as the Gaussian analysis of the spectrum. Three electronic transitions are observed in the near UV-region, 300–200 nm. The first, lowest energy, transition shows some vibration structures which characterize the lowest energy transition of pyridine molecule but have been red shifted in 2-azidopyridine to 256 nm, pyridine lowest energy transition is ~250 nm [18]. The spectrum (Fig. 1) shows a relatively weak band around 240 nm which appears as a long wavelength shoulder to a relatively strong band at ~215 nm. The extinction coefficient varies from 1.8×10^3 to 2×10^3 mol⁻¹ L cm⁻¹ indicating that the observed absorption bands correspond to allowed $\pi \rightarrow \pi^*$ transitions.

In cyclohexane, as a solvent, the general features of the spectrum did not vary and a general red shift is observed for all bands. The results shown in Fig. 1 indicate an apparent perturbation effect of the azide group on the energy levels of the parent molecule, pyridine. The spectrum of pyridine exhibits only one absorption band in the 300–200 nm region whereas that of 2-azidopyridine exhibits three well-defined electronic transitions in the same region. Extension of the π -system in pyridine nucleus by addition of the azide group as well as its electron-donating behaviour is beyond the variation of the spectrum of 2-azidopyridine from that of pyridine.

Azide \rightleftharpoons Tetrazole equilibrium is an established phenomenon, the value of the equilibrium constant and the factors which affect the position of the equilibrium has been discussed [19–23].

The spectrum of 2-azidopyridine in absolute ethanol as shown in Fig. 1, is structurally related to that of pyridine and differs completely from that of tetrazole. Sasaki et al. [24] reported tetrazolo [1,5-a] pyridine has two absorption bands: at 223 nm, $\epsilon = 2.68 \times 10^4$, and at 310 nm, $\epsilon = 6.10 \times 10^3$, which are totally different from the absorption bands of 2-azidopyridine.

Wentrup [25] concluded that tetrazolo [1,5-a] pyridines are completely stable in solution at 140 °C. The result of this work (Fig. 1) prove that in absolute ethanol and at room temperature

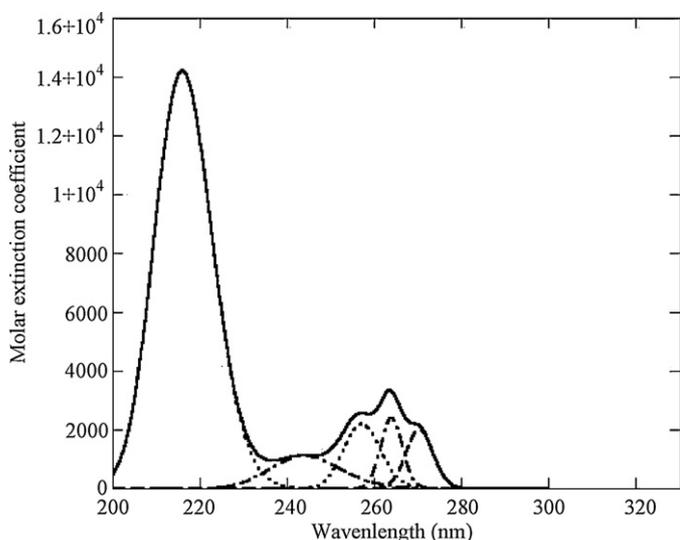


Fig. 1. Electronic absorption spectrum of 2-azidopyridine in absolute ethanol and the Gaussian analysis of the spectrum.

2-azidopyridine exists totally in the azide form, the equilibrium with tetrazole is not detectably established.

3.1.2. Solvent–solute interaction

The theory of solute–solvent interaction has been reviewed [26]. Solvation energy can be defined quantitatively as the energy of interaction between a solute and a solvent. The two important and commonly used formulations for solvent–solute interaction are the Born (point charge model) and Onsager (point dipole dielectric continuum model) formulations. In both models electric charges and lengths are combined to obtain the physical dimension of energy.

$$(i)(\text{Born}) \quad E_{\text{solv}}^{\text{ion}} = \frac{-q^2}{2a} F(D) = ML^2T^{-2} \quad (1)$$

$$(ii)(\text{Onsager}) \quad E_{\text{solv}}^{\text{dipol}} = \frac{-\mu^2}{2a^3} f(D) = ML^2T^{-2} \quad (2)$$

The solvent polarity functions $F(D)$ and $f(D)$ are dimensionless numbers as they represent the relative strength of the electric field experienced by the ion or dipole.

The reaction field model of solute–solvent interactions introduced by Onsager Eq. (2) is most widely used. In this model, a neutral dipolar molecule is a sphere of isotropic polarizability, α , and central point dipole moment, μ . The dipole produces an electric field which decreases with the third power of the distance r ,

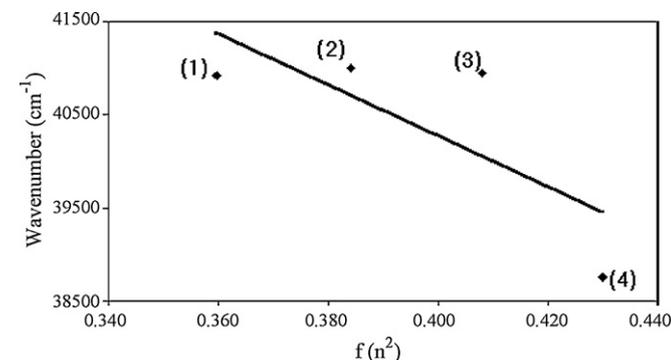


Fig. 2. Variation of band maximum of the highest-energy transition of 2-azidopyridine with refractive index of the solvent. The solvents are: (1) pentane, (2) iso-octane (3) cyclohexane, and (4) carbon tetrachloride.

Table 1

Band maxima, molar extinction coefficients, and oscillator strengths of 2-azido pyridine in different solvents

Solvent	λ_{max} (nm)	ϵ ($\text{mol}^{-1} \text{L cm}^{-1}$)	f
Ethanol absolute	216	14,200	0.22
	244	1,100	0.016
	265	2,400	10^{-2}
Acetonitrile	213	18,200	0.1
	241	1,700	0.026
	257	3,500	0.016
Methyl alcohol	214	5,000	0.043
	235	780	0.018
	257	3,500	0.022
Dioxane	216	3,750	0.035
	238	1,100	0.019
	256	3,100	10^{-2}
Water	209	7,700	0.04
	235	900	0.02
	257	3,790	0.029
Isopropyl alcohol	209	5,500	0.033
	238	400	0.086
	257	1,800	0.011
Dichloroethane	223	3,600	0.047
	244	4,600	0.11
	258	9,500	0.043
Cyclohexane	244	5,600	0.048
	252	1,880	0.00
	265	3,700	0.024
Iso-octane	244	800	0.007
	252	1,250	0.007
	256	2,400	0.017
Pentane	245	600	0.007
	252	900	0.005
	265	2,200	0.014
Carbon tetrachloride	258	2,300	10^{-3}
	265	2,300	0.016
	273	1,900	0.003
Diethyl ether	258	3,210	0.0002
	264	3,730	10^{-2}
	271	2,580	0.004

and this field has two separate effects on the surrounding solvent molecules: (a) induction polarization and (b) orientation polarization.

In case of induction polarization the solvent–solute interaction is given by

$$E_{\text{solv}} = \frac{-\mu_M}{a_M^3} f(n^2) \quad (3)$$

$$f(n^2) = \frac{2(n^2 - 1)}{(2n^2 + 1)} \quad (4)$$

where n is the refractive index and a_M is the radius of the spherical cavity which contains the solvent molecule.

For orientation polarization of the solvent dipoles the total solvation energy is then

$$E_{\text{solv}} = \frac{-\mu_M}{2a_M^3} [f(D) - f(n^2)] \quad (5)$$

$$f(D) = \frac{2(D - 1)}{2D + 1} \quad (6)$$

where D is the dielectric constant.

The electronic absorption spectra of 2-azidopyridine have been investigated in different solvents. The nature, type, intensity and position of the absorption bands may be significantly affected by

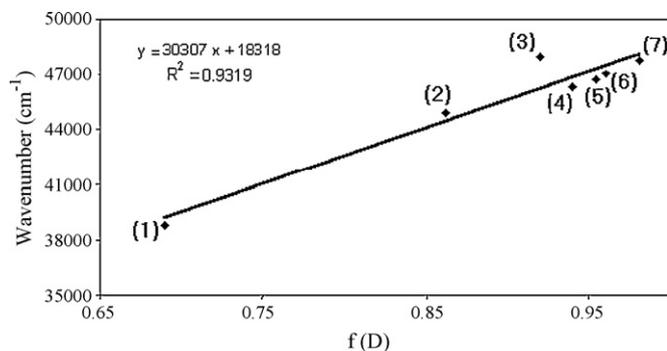


Fig. 3. Variation of band maximum of the highest-energy transition of 2-azidopyridine with the dielectric constant of the solvent. The solvents are: (1) diethylether, (2) dichloroethane, (3) isopropyl alc., (4) ethanol, (5) methanol, (6) acetonitrile, and (7) water.

the type of the solvent. Table 1 gives the values of λ_{\max} and molar extinction coefficient, ϵ , of 2-azidopyridine in different solvents. The shift of band maxima with solvent polarity is small indicating that the contribution of charge transfer configuration to the excited states is small. This result has been confirmed by MO calculations.

Solvent–solute interaction is dependent on the properties of both the solvent, polarity of the solute and the type of the electronic transition. The solvatochromic shifts are often used to assign the transition as $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ or a charge transfer one. The studied pyridine azides are polar compounds. The spectra have been investigated in polar and non-polar solvents. For truly non-polar solvents, only the expressions in $f(n^2)$ remain in the solvatochromic shift equation, Eq. (5). When there is a change in dipole moment on excitation the dipole induced dipole term becomes dominant. Fig. 2 shows the relation between λ_{\max} (cm^{-1}) of the highest energy electronic transition of 2-azidopyridine against $f(n^2)$ of the solvent, Eq. (4) for a number of a non-polar solvents. The linearity of the plot is generally quite satisfactory and the specific shifts are larger than due to dispersion interaction. Nevertheless, the slope is negative and gives $-\mu_M/a_M^3$.

Fig. 3 shows the relation between λ_{\max} (cm^{-1}) of the highest energy electronic transition of 2-azidopyridine against the solvent polarity function $f(D)$, for a number of polar solvents of the same refractive index. According to the expression of solvatochromic shift of dipolar solute in polar solvents, these shifts result from the dipole–dipole interaction only and they are the strongest non-specific intermolecular forces. The slope of Fig. 3 is positive indicating that the E_{solv} is negative. Hence one concludes that the main solvent–solute interaction is a dipole–dipole interaction.

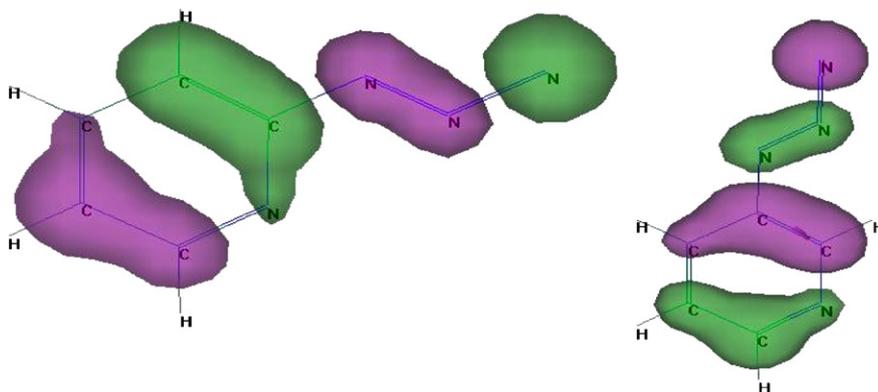


Fig. 5. HOMOs of 2- and of 3-azidopyridines.

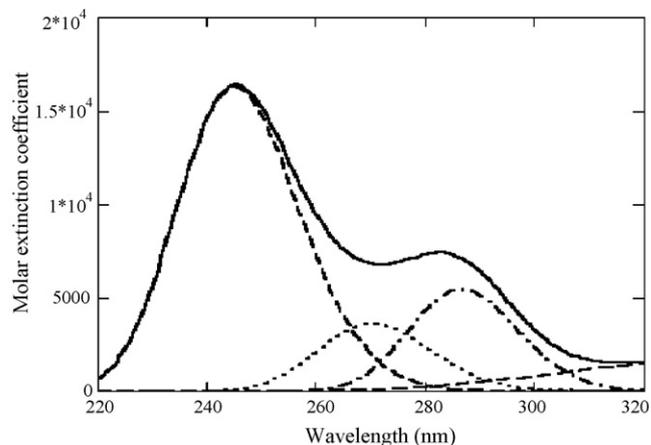


Fig. 4. Electronic absorption spectrum of 3-azidopyridine in absolute ethanol and its Gaussian analysis.

3.2. 3-Azidopyridine

The electronic absorption spectrum of 3-azidopyridine in absolute ethanol is shown in Fig. 4. Gaussian analysis of the spectrum indicates the presence of two overlapping transitions with band maxima at 287 nm ($\epsilon = 4980$) and at 270 nm ($\epsilon = 3600$). The highest energy transition of 3-azidopyridine has a band maximum at 245 nm ($\epsilon = 16,300$). Band intensity indicates that all the observed transitions correspond to allowed $\pi \rightarrow \pi^*$ transitions.

The spectrum of 3-azidopyridine differs basically from the spectra of pyridine and from those of mono-substituted pyridines. The longest wavelength transition of pyridine with its characteristic vibrational structure is not observed in the spectrum of 3-azidopyridine while it persists in the spectrum of 2-azidopyridine. This reveals that $\pi \rightarrow \pi$ interaction between the pyridine nucleus and the azide group attached to C(3) in pyridine ring is much stronger than what exists in 2-azidopyridine. A comparison of contour map diagrams, obtained by HyperChem release 2 for windows 1991, for the HOMO's of the two isomers (Fig. 5) confirm this conclusion [27]. As a result, all electronic transitions of 3-azidopyridine are red shifted as compared to those of the 2-isomer. This interpretation agrees with the concept of the resonance theory. The endocyclic N-atom is an electron withdrawing and its electron interaction is the most with the meta position.

The absorption spectrum of 3-azidopyridine using cyclohexane as a solvent shows three electronic transitions which show negligible band shift with solvent polarity, a result which reflects negligible contribution of CT configurations to the excited states.

Table 2
Band maxima, molar extinction coefficients and oscillator strengths of 3-azido pyridine in different solvents

Solvent	λ_{\max} (nm)	ϵ ($\text{mol}^{-1} \text{L cm}^{-1}$)	f
Ethanol absolute	245	16,300	0.38
	270	3,600	0.034
	287	4,980	0.065
Acetonitrile	246	18,750	0.44
	270	3,000	0.036
	284	55,000	0.072
Methyl alcohol	246	76,900	1.667
	267	1,400	0.164
	284	21,200	0.276
Dioxane	248	32,500	0.65
	270	5,300	0.06
	285	10,000	0.12
Water	246	11,500	0.27
	270	1,400	0.02
	285	3,800	0.05
Isopropyl alcohol	246	47,500	1.2
	273	3,700	0.07
	285	14,800	0.18
Dichloroethane	247	69,000	1.179
	266	17,250	0.201
	284	20,900	0.256
Cyclohexane	246	6,150	0.15
	273	1,150	0.01
	287	1,700	0.018
Iso-octane	246	6,300	0.16
	274	1,330	0.01
	287	1,700	0.018
Pentane	248	6,150	0.15
	273	1,150	0.01
	287	1,700	0.017
Carbon tetrachloride	259	5,100	0.01
	270	2,900	0.032
	287	2,360	0.03
Diethyl ether	247	7,300	0.11
	267	1,830	0.02
	283	2,340	0.03

Table 2 gives the values of band maxima and molar extinction coefficients of the observed transitions of 3-azidopyridine. Fig. 6 shows the variation of band maximum of the highest energy electronic transition of 3-azidopyridine with solvent refractive index as given by the function $f(n^2)$. The linearity of the plot is satisfactory. The slope of the plot is negative and is of small value which

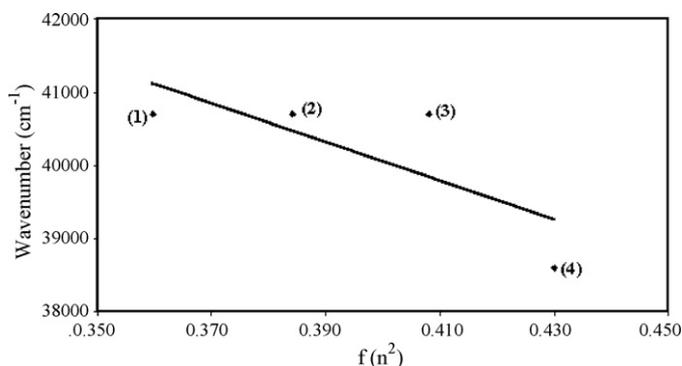


Fig. 6. Variation of band maximum of the highest-energy transition of 3-azidopyridine with refractive index of the solvent. The solvents are: (1) pentane, (2) iso-octane (3) cyclohexane, and (4) carbon tetrachloride.

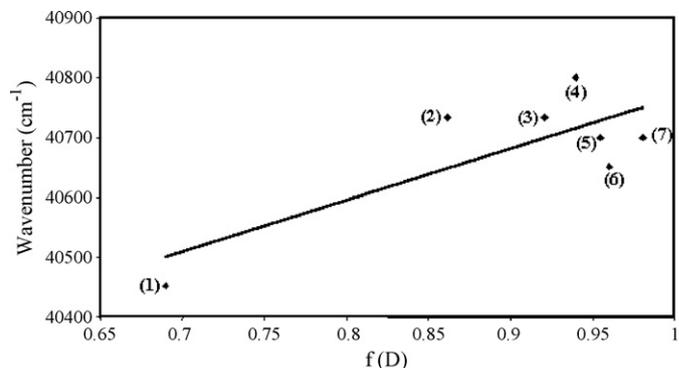


Fig. 7. The variation of band maximum of the highest-energy transition of 3-azidopyridine with dielectric constant of the solvent. The solvents are: (1) diethylether, (2) dichloroethane, (3) isopropyl alc., (4) ethanol, (5) methanol, (6) acetonitrile, and (7) water.

reflects a weak solvent–solute interaction due to the variation of the solvent refractive index.

Fig. 7 shows the relation between λ_{\max} of the highest energy transition of 3-azidopyridine and Onsager solvent polarity function $f(D)$ using solvents of the same refractive index. The linearity of the plot is satisfactory. The plot has a positive slope and E_{solvent} is negative. Figs. 6 and 7 indicate that the strongest solvent–solute interaction is the dipole–dipole interaction.

3.3. 4-Azidopyridine

The electronic absorption spectrum of 4-azidopyridine using absolute ethanol as a solvent is shown in Fig. 8. A broad shoulder is resolved to two overlapping transitions with maxima at 295 nm ($\epsilon = 500$) and at 277 nm ($\epsilon = 470$). The strongest transition, $\epsilon = 1860$, has a band maximum around 250 nm. A fourth transition that was not observed in the spectra of 2- and 3-azidopyridines appears at 230 nm, $\epsilon = 810$. In spite of the relative low intensity of all the observed transitions of 4-azidopyridine yet none of them corresponds to an $n \rightarrow \pi^*$ transition as is confirmed by the absence of blue shift of band maxima with solvent polarity. The low intensity of the observed bands of 4-azidopyridine is related to the high symmetry of the molecule, approximately C_{2v} point group and some of the transitions are symmetry forbidden.

A comparison of the values of band maxima of 2-, 3-, and 4-azidopyridines is instructive (Table 3). The results indicate that the $\pi \rightarrow \pi$ electron interaction between the azide group and the pyridine ring is the strongest in the case of 3-azidopyridine. The most

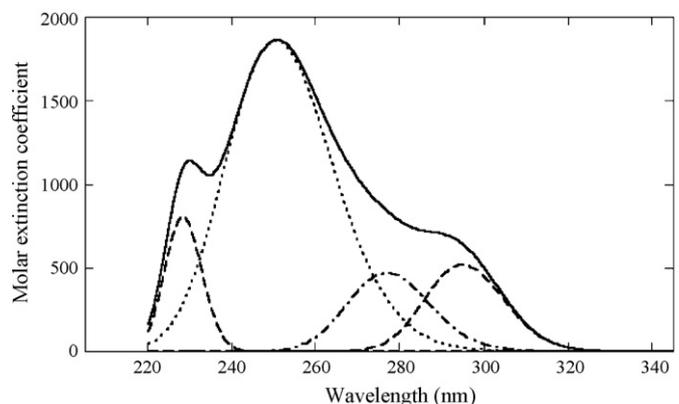


Fig. 8. Electronic absorption spectrum of 4-azidopyridine in absolute ethanol and its Gaussian analysis.

Table 3

Band maxima and band intensity of the electronic transition of the three azidopyridines using cyclohexane as a solvent

2-Azidopyridine	3-Azidopyridine	4-Azidopyridine
244(5600) ^a	246(6150)	229(710)
252(1880)	273(1150)	249(1190)
265(3700)	287(1700)	277(400)
		292(300)

^a Molar extinction coefficient.

intense bands are observed in the spectrum of 3-azidopyridine and the least intense ones are observed in the spectrum of the 4-isomer.

The spectrum of 4-azidopyridine has been investigated in a number of solvents (Table 4). Fig. 9 shows the relation between

Table 4

Band maxima, molar extinction coefficients, and oscillator strengths of 4-azido pyridine in different solvents

Solvent	λ_{\max} (nm)	ϵ (mol ⁻¹ Lcm ⁻¹)	f
	228	810	0.006
Ethanol absolute	251	1,860	0.045
	277	470	0.006
	295	520	0.06
Acetonitrile	226	680	0.006
	246	1,300	0.034
	284	450	0.008
	345	35	0.0001
Methyl alcohol	229	6,200	0.06
	253	13,100	0.306
	280	34,100	0.05
	295	4,100	0.05
Dioxane	215	230	0.027
	246	505	0.014
	277	108	0.001
	292	120	0.001
Water	228	24,500	0.03
	258	5,800	0.15
	296	1,500	0.02
	323	350	0.003
Isopropyl alcohol	228	1,400	0.011
	249	3,400	0.085
	277	800	0.003
	295	1,000	0.012
Dichloroethane	229	6,900	0.112
	253	11,700	0.204
	275	4,900	0.053
	293	4,100	0.044
Cyclohexane	229	710	0.005
	249	1,190	0.023
	277	400	0.005
	292	300	0.004
Iso-octane	228	3,600	0.02
	248	6,500	0.13
	283	2,670	0.045
	323	80	0.009
Pentane	227	3,700	0.03
	248	6,600	0.12
	270	1,600	0.013
	286	2,300	0.028
Carbon tetrachloride	260	950	0.005
	276	560	0.007
	293	440	0.005
	333	12	0.0002
Diethyl ether	247	1,400	0.023
	270	5,600	0.006
	289	425	0.005
	333	2	0.0

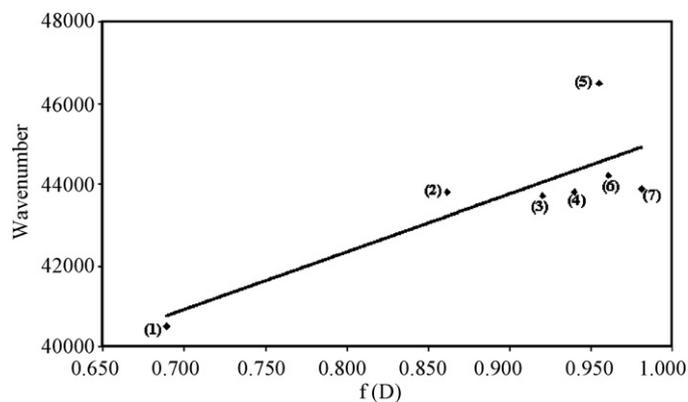


Fig. 9. Variation of band maximum of the highest-energy transition of 3-azidopyridine with dielectric constant of the solvent. The solvents are: (1) diethylether, (2) dichloroethane, (3) isopropyl alc., (4) ethanol, (5) methanol, (6) acetonitrile, and (7) water.

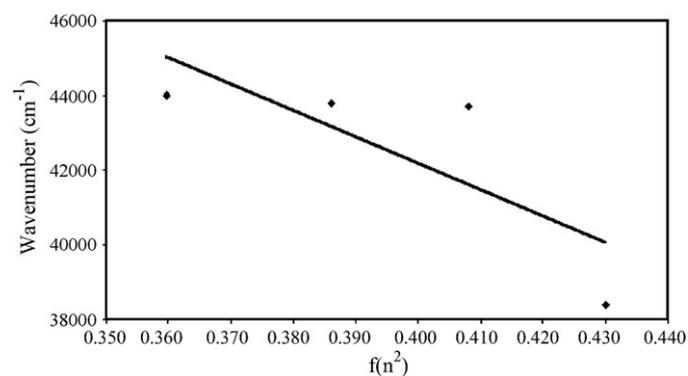


Fig. 10. The variation of band maximum of the highest-energy transition of 3-azidopyridine with refractive index of the solvent. The solvents are: (1) pentane, (2) iso-octane (3) cyclohexane, and (4) carbontetrachloride.

the values of band maximum of the highest energy electronic transition in 4-azidopyridine and the solvent polarity function $f(D)$. A positive and steep slope of the plot indicate a strong solvent–solute interaction. Band maximum shifts to higher wave number with the increase of solvent polarity which means a strong dipole–dipole interaction.

Fig. 10 shows the relation between band maximum of the highest energy transition of 4-azidopyridine and the refractive index of the solvent as given by the function $f(n^2)$. The linearity of the plot is clear but the slope is weak indicating a weak solvent–solute interaction with the variation of the refractive index of non-polar solvents.

4. Conclusion

The extent of the perturbation effect of the azide group, which is generally an electron donor, varies according to the position of the azide group in the pyridine ring. Results at hand indicate that the strongest perturbation exists in the 3-azido isomer and the least one exists in the 2-azido isomer. The results obtained in this work agree with the predictions of the resonance theory. The spectra of azidopyridines differ basically from those of pyridine or substituted pyridine with respect to both band maxima and band intensity. The lowest-energy electronic transition of pyridine persists in the spectra of 2-azidopyridine but with different values of band maxima and band intensity. Overlapping transitions are clear in the

spectra of azidopyridines and Gaussian analysis yields a nice resolved spectrum.

In spite of the fact that the molecule, azidopyridine, contains two pairs of non-bonding electrons occupying the sp^2 hybrids on the endocyclic N-atom and on the N-azide atom attached to pyridine ring, yet none of the observed transitions observed in the spectra of azidopyridines is assigned to an $n \rightarrow \pi^*$ transitions, these are overlapped with the stronger $\pi \rightarrow \pi^*$ ones.

Solvent-solute interactions affect the electronic transitions, mainly, due to dipole-dipole interaction and dispersion interaction. According to Onsager model the results of this work showed a stronger dipole-dipole interaction between azidopyridines and the solvent through the orientation polarization of the solvent dipoles. The induction polarization of solvent dipoles has a negligible effect on the electronic spectrum of azidopyridines.

Azide \rightleftharpoons tetrazole equilibrium is an established phenomenon. The spectra observed in this work confirm that tetrazole is not detected at the studied conditions.

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