Spectrophotometric Study of Intermolecular Hydrogen Bonds and Proton Transfer Complexes Between 1,2-Dihydroxyanthraquinone and Some Aliphatic Amines in Methanol and Acetonitrile

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Intermolecular hydrogen bonds (HB) and proton transfer (PT) complexes between 1,2-dihydroxyanthraqunone (alizarin-AZ) and some aliphatic amines including propylamine (PA), triethylamine (TEA), and pyrrolidine (PR) have been investigated spectrophotometrically in methanol (MeOH) and acetonitrile (MeCN). The formation constants of the proton transfer reactions (K_{PT}) have been estimated utilizing the minimum−maximum absorbances method. It has been found that K_{PT} was lower in MeCN. On the other hand, K_{PT} was greater in MeOH. Job's method of continuous variations and molar ratio photometric titrations were used to identify the composition of the PT complexes formed. On the basis of the rapidity of the PT reaction, a simple and accurate spectrophotometric method for determination of AZ was proposed. Beer's law was obeyed in the concentration range ($1.0 \cdot 10^{-5}$ to $1.0 \cdot 10^{-4}$) $mol \cdot L^{-1}$ in methanol and ($1.0 \cdot 10^{-5}$ to $2.0 \cdot 10^{-4}$) $mol \cdot L^{-1}$ in acetonitrile with excellent correlation coefficients. The recovery percentages ranged from (99.87 to 100.80) %, with relative standard deviations (RSD) ranging from (0.91 to 1.75).

Introduction

Hydrogen bonding is defined as the attraction between a donor hydrogen atom and an electronegative hydrogen acceptor atom that usually has at least one lone pair of electrons.[1] Hydrogen bonds are responsible for maintaining small polar molecules like water and alcohols in liquid state at room temperature.[2,3] They are responsible for molecular recognition in DNA and determine to a large extent the secondary structure of proteins. Moreover, hydrogen bonding interactions play an important role in the catalytic reactivity of enzymes.[4]

The applications of H-bonding have been widely extended to various thermodynamic processes of industrial importance and fundamental research.[5−7] A recent application is in enhancing the performance of liquid crystal displays (LCDs) by the formation of a hydrogen bond between the liquid crystal and dichroic dye dissolved in it.[8−10]

It has been reported that hydroxyanthraquinone derivatives are known to be photosensitive and are used for photodynamic therapy such as antitumor drug.[11−14] In particular, dihydroxyanthraquinones have important applications as a prominent family of pharmaceutically active and biologically relevant chromophores.[15,16] Moreover, dihydroxyanthraquinones are used as analytical reagents for the determination of metals and in electrochemistry.[17,18]

Alizarin (AZ) is a component of food, which can act as an anticancer agent. It is also used as a dye and a chemical reagent for data recording and storage material.[19] In addition, AZ is extensively used as an intermediate in the production of optical brighteners and fluorescent whitening agents.

Due to the above biological importance and industrial applications of alizarine, we here report our findings on the intermolecular H-bonds and proton transfer complexes between AZ as a hydrogen bond donor (HBD) and some aliphatic amines including propylamine, triethylamine, and pyrrolidine as hydrogen bond acceptors (HBA) in both polar protic and polar aprotic solvents, methanol (MeOH) and acetonitrile (MeCN), respectively. These amines were selected based on their high basicities and abilities to form proton transfer complexes with various proton donors. Also, the mechanism of the formation of the PT complexes including MeOH or MeCN molecules was illustrated. In addition, the calculations of the formation constants of the proton transfer reactions (K_{PT}) were presented. In this work, a simple, rapid, and sensitive spectrophotometric method for determination of AZ was described.

Experimental Section

Apparatus. All spectrophotometric measurements were carried out using a spectrophotometer (UV-1601 Shimadzu, Japan) with spectroscopic software, version 3.7, and with silica cells of 1 cm thickness in the wavelength range (200 to 800) nm. The temperature gives uncertainty ± 0.1 °C with a Shimadzu TCC-ZUOA temperature controller unit.

Materials. All chemicals used were of analytical grade. Alizarin was supplied by BDH, and propylamine, triethylamine, and pyrrolidine were supplied by Acros organic. Methanol was supplied by Panreac, and acetonitrile was supplied by Lab-Scan.

Calculation of the Formation Constants K_{PT}. For the purpose of UV−vis spectral determination of the formation constants (K_{PT}), the minimum−maximum absorbances method was applied according to the following procedure. An amount of 1 mL of freshly prepared standard stock solutions of alizarin in methanol or acetonitrile ($1.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$) was transferred into ten 10 mL calibrated flasks. To each of these were added different concentrations of freshly prepared amine standard stock solutions: $1.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$ of propylamine, triethylamine, and pyrrolidine in methanol, $5.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$ of propylamine and

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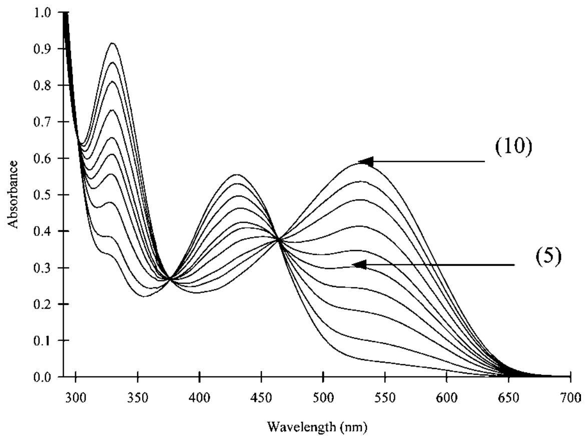


Figure 1. Electronic spectra of the PT complex formation between [10^{-4} mol·L^{-1}] AZ and various concentrations of PA in MeOH: 1, 0.0; 2, 1.0·10^{-5}; 3, 2.5·10^{-5}; 4, 3.5·10^{-5}; 5, 5.0·10^{-5}; 6, 6.0·10^{-5}; 7, 7.5·10^{-5}; 8, 1.0·10^{-4}; 9, 1.2·10^{-4}; 10, 1.5·10^{-4} mol·L^{-1}.

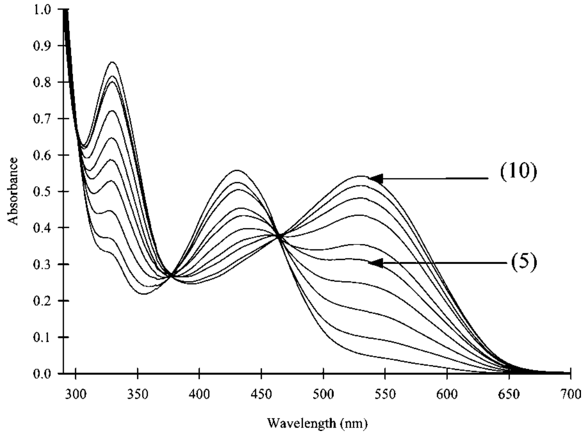


Figure 2. Electronic spectra of the PT complex formation between [10^{-4} mol·L^{-1}] AZ and various concentrations of TEA in MeOH: 1, 0.0; 2, 1.0·10^{-5}; 3, 2.5·10^{-5}; 4, 5.0·10^{-5}; 5, 7.0·10^{-5}; 6, 1.0·10^{-4}; 7, 1.5·10^{-4}; 8, 2.0·10^{-4}; 9, 2.5·10^{-4}; 10, 3.0·10^{-4} mol·L^{-1}.

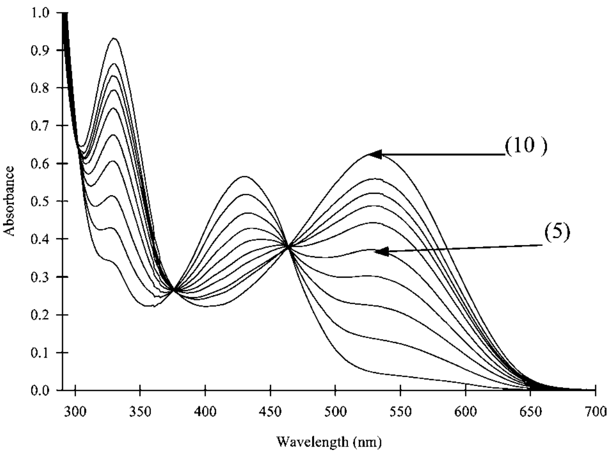


Figure 3. Electronic spectra of the PT complex formation between [10^{-4} mol·L^{-1}] AZ and various concentrations of PR in MeOH: 1, 0.0; 2, 1.0·10^{-5}; 3, 2.0·10^{-5}; 4, 3.0·10^{-5}; 5, 4.0·10^{-5}; 6, 5.0·10^{-5}; 7, 6.0·10^{-5}; 8, 7.0·10^{-5}; 9, 8.5·10^{-5}; 10, 1.0·10^{-4} mol·L^{-1}.

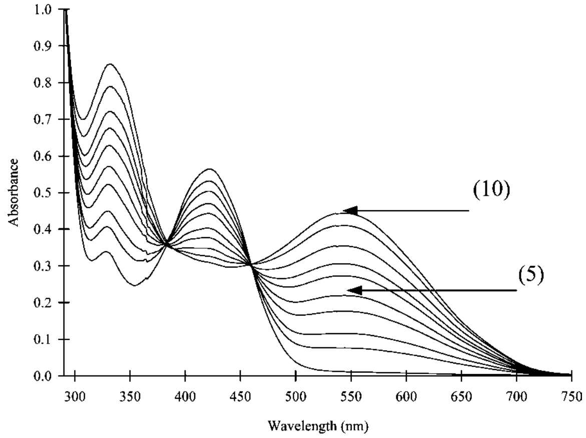


Figure 4. Electronic spectra of the PT complex formation between [10^{-4} mol·L^{-1}] AZ and various concentrations of PA in MeCN: 1, 0.0; 2, 5.0·10^{-4}; 3, 1.0·10^{-3}; 4, 2.0·10^{-3}; 5, 3.0·10^{-3}; 6, 5.0·10^{-3}; 7, 7.0·10^{-3}; 8, 1.0·10^{-2}; 9, 1.5·10^{-2}; 10, 2.0·10^{-2} mol·L^{-1}.

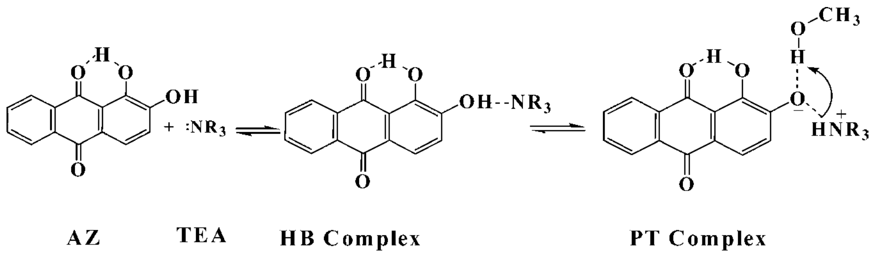
triethylamine, and 5.0·10^{-3} mol·L^{-1} of pyrrolidine in acetonitrile. The absorbance of the mixture solutions was recorded against a solvent blank. The lowest amine concentration led to the minimum absorbance of the PT complex ($A_{\mathrm{min.}}$). The concentration of the amine was increased gradually, and the absorbance was recorded at the maximum absorption band of the PT complex ($A_{\mathrm{mix.}}$) until the highest and constant absorbance of the formed PT complex was obtained ($A_{\mathrm{max.}}$). The PT formation constants (K_{PT}) were estimated as given by the following equation[20−22]

$$A_{\mathrm{max.}} = A_{\mathrm{mix.}} + \frac{A_{\mathrm{mix.}} - A_{\mathrm{min.}}}{K_{\mathrm{PT}} C_{\mathrm{amine}}} \qquad (1)$$

where $A_{\mathrm{max.}}$ and $A_{\mathrm{min.}}$ are the maximum and minimum absorbances of the proton transfer complex. $A_{\mathrm{mix.}}$ is the complex absorbance between $A_{\mathrm{max.}}$ and $A_{\mathrm{min.}}$. C_{amine} is the concentration of the added amine in moles per liter. The set of equilibrium constants was averaged to extract the central K_{PT} value with minimum error.

Spectrophotometric Titrations. Spectrophotometric titrations were performed to determine the course of the reaction in MeCN and MeOH between AZ and amines. These measurements were based on the absorption band of the formed PT complexes according to the following procedure: the concentration of AZ was kept constant at 2.5·10^{-4} mol·L^{-1} where that of the amine was changed from (5.0·10^{-5} to 5.0·10^{-4}) mol·L^{-1}.The HBA:HBD molar ratio obtained in this case varied from (0.2 to 2.0). The peak absorbances that appeared in the spectra that were assigned to the formed PT complexes were measured and plotted

Scheme 1. Proton Transfer Reaction in Methanol



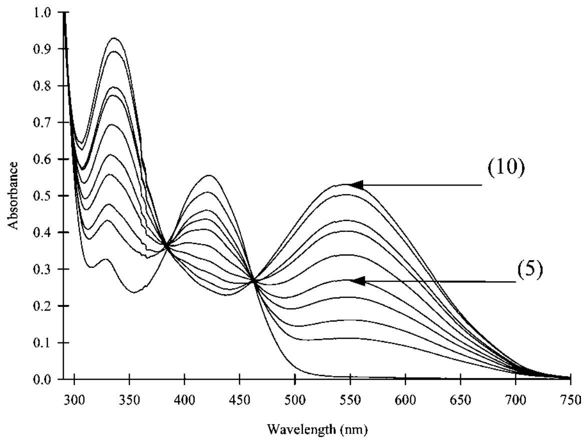


Figure 5. Electronic spectra of the PT complex formation between [10^{-4} $mol \cdot L^{-1}$] AZ and various concentrations of TEA in MeCN: 1, 0.0; 2, $5.0 \cdot 10^{-4}$; 3, $1.0 \cdot 10^{-3}$; 4, $2.0 \cdot 10^{-3}$; 5, $3.0 \cdot 10^{-3}$; 6, $5.0 \cdot 10^{-3}$; 7, $8.0 \cdot 10^{-3}$; 8, $1.0 \cdot 10^{-2}$; 9, $1.5 \cdot 10^{-2}$; 10, $2.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$.

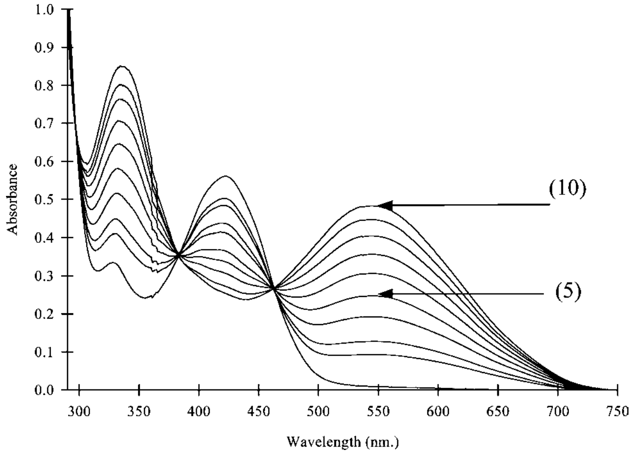


Figure 6. Electronic spectra of the PT complex formation between [10^{-4} $mol \cdot L^{-1}$] AZ and various concentrations of PR in MeCN: 1, 0.0; 2, $5.0 \cdot 10^{-5}$; 3, $1.0 \cdot 10^{-4}$; 4, $2.0 \cdot 10^{-4}$; 5, $3.0 \cdot 10^{-4}$; 6, $5.0 \cdot 10^{-4}$; 7, $7.0 \cdot 10^{-4}$; 8, $1.0 \cdot 10^{-3}$; 9, $1.5 \cdot 10^{-3}$; 10, $2.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$.

Table 1. pK_a of Amines, Concentration Range, and K_{PT} in Methanol at 25 °C

amine	pK_a	concentration range $mol \cdot L^{-1}$	$\lambda_{max(PT)}$ nm	$K_{PT} \cdot 10^{-3}$ $mol \cdot L^{-1}$
propylamine	10.35	$1.0 \cdot 10^{-5}$ to $1.5 \cdot 10^{-4}$	530	29.1
triethylamine	10.75	$1.0 \cdot 10^{-5}$ to $3.0 \cdot 10^{-4}$	530	25.2
pyrrolidine	11.31	$1.0 \cdot 10^{-5}$ to $1.0 \cdot 10^{-4}$	530	44.1

as a function of the molar ratio HBA:HBD according to the known method.[23]

Results and Discussion

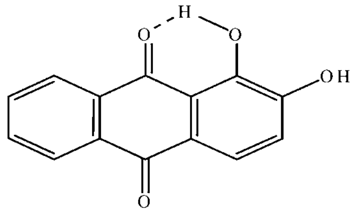
The molecular structure of AZ is given in formula 1, where the intramolecular hydrogen bond is the most stable one in the ground state. The lowest electronically excited state of unsubstituted anthraquinones lies in the UV region because of the $n-\pi^*$ characters.[14] However, the $\pi-\pi^*$ state becomes the lowest excited when an anthraquinone is substituted with an OH group.[13]

Table 2. pK_a of Amines, Concentration Range, and K_{PT} in Acetonitrile at 25 °C

amine	pK_a	concentration range $mol \cdot L^{-1}$	$\lambda_{max(PT)}$ nm	$K_{PT} \cdot 10^{-3}$ $mol \cdot L^{-1}$
propylamine	10.35	$5.0 \cdot 10^{-4}$ to $2.0 \cdot 10^{-2}$	545	0.38
triethylamine	10.75	$5.0 \cdot 10^{-4}$ to $2.0 \cdot 10^{-2}$	545	0.48
pyrrolidine	11.31	$5.0 \cdot 10^{-5}$ to $2.0 \cdot 10^{-3}$	545	4.33

Table 3. Concentration of Amines Corresponding to 50 % PT (*C*) and Slopes (*s*)

	MeOH		MeCN	
amine	$C/mol \cdot L^{-1}$	$s \cdot 10^{-3}$	$C/mol \cdot L^{-1}$	$s \cdot 10^{-3}$
propylamine	$6.77 \cdot 10^{-5}$	14.09 ± 1.43	$1.15 \cdot 10^{-2}$	0.07
triethylamine	$1.33 \cdot 10^{-4}$	5.77 ± 0.81	$6.92 \cdot 10^{-3}$	0.11
pyrrolidine	$4.12 \cdot 10^{-5}$	23.21 ± 1.82	$8.22 \cdot 10^{-4}$	0.93



1,2-dihydroxyanthraquinone (Alizarin)

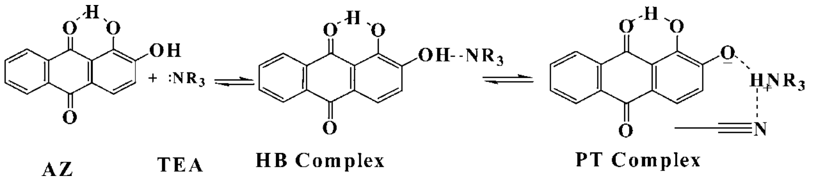
Formula 1

Electronic Spectra. The electronic spectra of the hydrogen bonding interaction between $1.0 \cdot 10^{-4}$ $mol \cdot L^{-1}$ AZ and various amine concentrations were presented in Figures 1 to 3 at 25 °C in methanol. The electronic spectra revealed two absorption bands at (430 and 530) nm which could be assigned to the $\pi-\pi^*$ transition of the molecular hydrogen bonded (HB) and proton transfer (PT) complexes between AZ and amines, respectively. Two isosbestic points at (375 and 464) nm were observed in the electronic spectra in Figures 1 to 3 confirming the presence of two equilibria including HB and PT complexes in methanol (Scheme 1).

The electronic absorption spectra of the hydrogen bonding interaction between $1.0 \cdot 10^{-4}$ $mol \cdot L^{-1}$ AZ and the amines at 25 °C in acetonitrile were presented in Figures 4 to 6. The PT bands appeared at 545 nm, while the HB one appeared at 430 nm, respectively. Two isosbestic points were recorded in Figures 4 to 6 at (383 and 460) nm, respectively, confirming the presence of two equilibria including HB and PT complexes in acetonitrile (Scheme 2).

Proton Transfer Formation Constants (K_{PT}). The PT formation constants (K_{PT}) were computed using the minimum−maximum absorbances method. The concentration range, aqueous pK_a of amines, and K_{PT} values in methanol and acetonitrile were compiled in Tables 1 and 2. One observes from Tables 1 and 2 the higher values of K_{PT} in methanol than in acetonitrile

Scheme 2. Proton Transfer Reaction in Acetonitrile



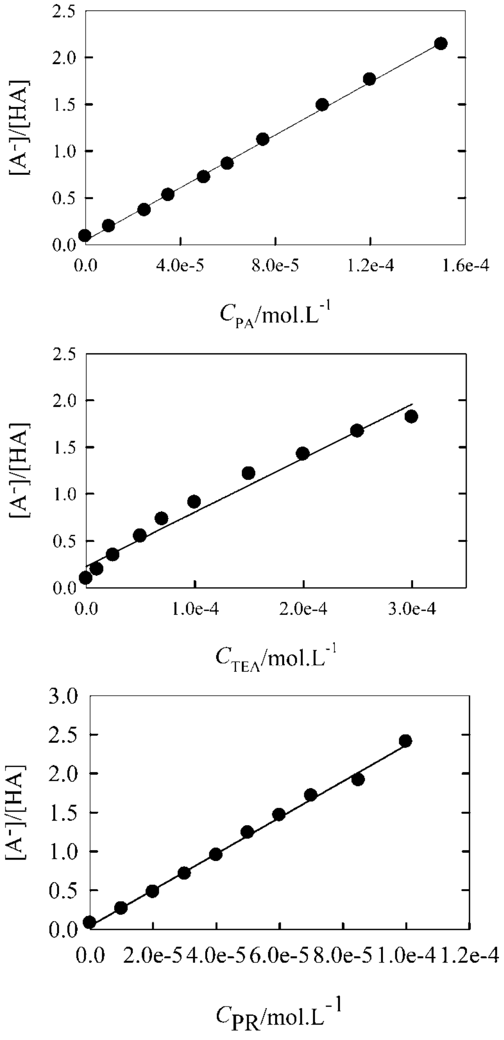


Figure 7. Correlation between [A$^-$]/[HA] and amine concentration for the PT complexes in MeOH.

confirming the higher stability of the formed PT complexes in methanol than in acetonitrile. It is also observed from Tables 1 and 2 that K_{PT} values were going in harmony with the amine pK_a values in acetonitrile. On the other hand, K_{PT} for the alizarin–propylamine complex recorded a higher value than the alizarin–triethylamine one in methanol although triethylamine has a higher pK_a than propylamine. This result could be interpreted on the basis that methanol exhibited dual functions in the studied proton transfer reactions. The first one is that methanol forms cooperative hydrogen bonding with the hydroxyl group of alizarine that increases its acidity[24] (Scheme 1). The second one is that methanol interacts with propylamine and pyrrolidine through a short-range solvation effect.[24] This effect shifts the lone pair of electrons of the N–H bond toward the nitrogen center and increases its basicity. On the other hand, acetontrile binds the alizarine OH through intermolecular hydrogen bonding which retards the proton transfer reaction of AZ with amines.[25] In addition, MeCN molecules can form a dimer through self-association owing to strong dipole–dipole interaction between these molecules leading to a small effective dipole moment and synergistic behavior.[26,27] All these facts led to higher K_{PT} values in methanol than in acetonitrile.

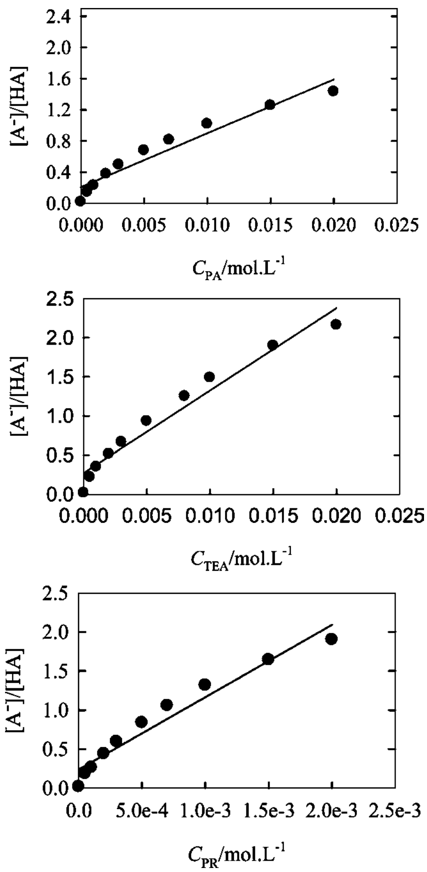


Figure 8. Correlation between [A$^-$]/[HA] and amine concentration for the PT complexes in MeCN.

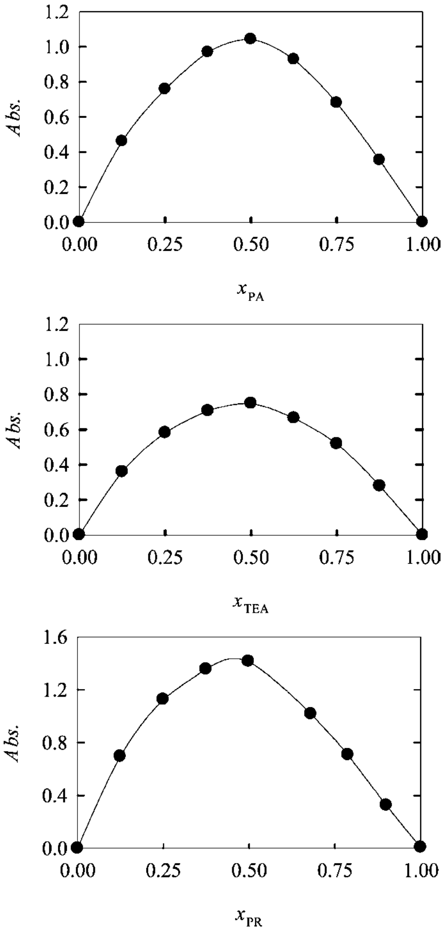


Figure 9. Continuous variation plots for the PT complexes in MeOH.

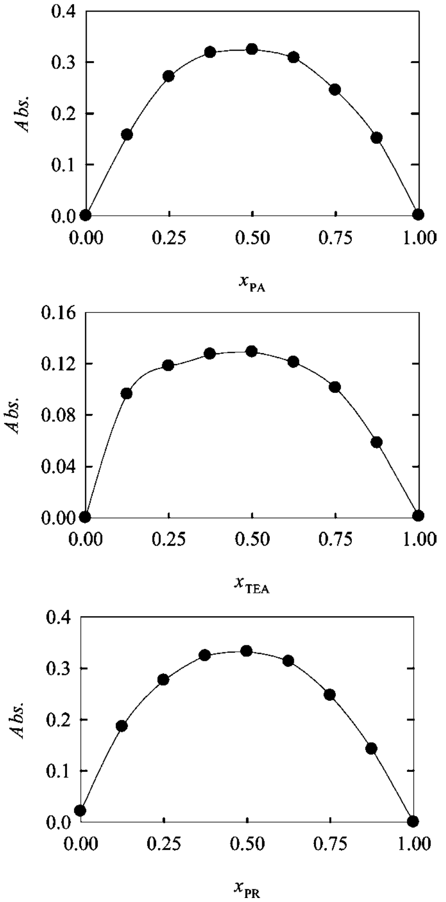


Figure 10. Continuous variation plots for the PT complexes in MeCN.

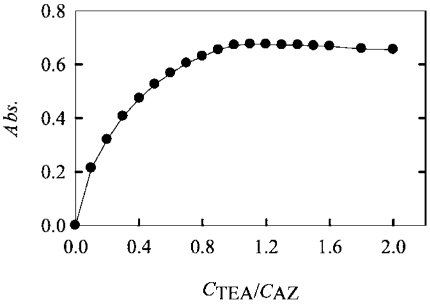


Figure 11. Photometric titration plot for the PT complex between AZ and TEA in MeOH.

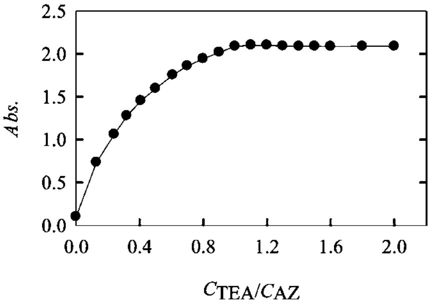


Figure 12. Photometric titration plot for the PT complex between AZ and TEA in MeCN.

More available data prove the existence of a double minimum potential[28,29] in solution representing the HB and PT complexes.

$$\underset{\text{HB}}{\text{OH.......N}} \rightleftharpoons \underset{\text{PT}}{\text{O}^{-}\text{.......H}^{+}\text{N}}$$

Consequently, it seems interesting to compare the heights of the energy barrier separating the two potential minima in MeOH and MeCN as follows: Construct the diagram correlating [A$^-$]/[HA] with the amine concentrations where [A$^-$] and [HA] are the absorbances of the PT and HB forms, respectively. Estimate the concentration required to obtain 50 % PT at which [A$^-$]/[HA] equals one. Compare the slopes of the fitted least-squares straight line and the concentrations required to reach 50 % PT in MeOH and MeCN. The data are compiled in Table 3 and depicted graphically in Figures 7 and 8. One can observe from Table 3 that the concentrations required to reach 50 % PT are smaller in MeOH than in MeCN, while the slopes of the fitted straight lines in MeOH reached larger values in MeOH than in MeCN for all the formed PT complexes.

An important observation in Figure 8 was the curvature in the plot especially at concentrations lower than 0.005 mol·L^{-1} which confirms the disturbance of the proton transfer process in MeCN. In addition, the dissociation of AZ in methanol in the presence of a base is favored over dissociation in acetonitrile.

Composition of the Formed PT Complexes. The molar composition of the PT complex between AZ and amines was determined by Job's method of continuous variations,[30] which

Table 4. Quantification Parameters of the PT Complexes

	MeOH			MeCN		
parameters	PA	TEA	PR	PA	TEA	PR
Beer's law limits/mol·L^{-1}	1.0·10^{-5} to 8.0·10^{-5}	1.0·10^{-5} to 1.0·10^{-4}	1.0·10^{-5} to 1.0·10^{-4}	1.0·10^{-5} to 1.0·10^{-4}	1.0·10^{-5} to 2.0·10^{-4}	1.0·10^{-5} to 1.0·10^{-4}
limit of detection/mol·L^{-1}	7.79·10^{-6}	1.07·10^{-5}	3.34·10^{-6}	6.13·10^{-6}	5.21·10^{-6}	1.45·10^{-6}
limit of quantification/mol·L^{-1}	2.60·10^{-5}	3.56·10^{-5}	1.11·10^{-5}	2.04·10^{-5}	1.74·10^{-5}	4.86·10^{-6}
molar absorptivity/L·mol^{-1}·mL^{-1}	4624	3627	6092	3081	4183	4060
regression equation[a]						
intercept, *a*	0.02	0.04	0.02	0.02	0.01	0.01
slope, *b*	4624	3627	6092	3081	4183	4060
confidence interval of intercept, α	0.02 ± 1.0·10^{-2}	0. 04 ± 1.0·10^{-2}	0. 01 ± 5.2·10^{-3}	0.02 ± 4.9·10^{-3}	0.01 ± 4.3·10^{-3}	0.01 ± 1.5·10^{-3}
confidence interval of slope, *β*	4624 ± 209	3627 ± 166	6092 ± 86	3081 ± 81	4183 ± 46	4060 ± 25
correlation coefficient, *r*	0.99	0.99	0.99	0.99	0.99	0.99

[a] $Y = a + bX$, where Y is the absorbance for concentration, X in mol·L^{-1}.

Table 5. Evaluation of the Uncertainty of the Method[a]

amine	average of rec. (%)	S.E.	RSD, % ($n = 10$)	average of $\|Y - F\|$	$\pm (tS/\sqrt{n})$
MeOH					
propylamine	99.87	0.55	1.75	0.17	± 1.30
triethylamine	100.60	0.34	1.08	0.17	± 0.77
pyrrolidine	100.41	0.33	1.03	0.12	± 0.74
MeCN					
propylamine	100.67	0.36	1.13	0.17	± 0.81
triethylamine	100.79	0.29	0.91	0.11	± 0.66
pyrrolidine	100.80	0.33	1.03	0.09	± 0.74

[a] Y = amount taken; F = amount found from regression equation; t = 2.262 for n = 10 at 95 % confidence level; S.E. = standard error; RSD = relative standard deviation; S = standard deviation.

was found to be 1:1 (HBA:HBD) as shown in Figures 9 and 10 which correlate the mole fraction of amine (x) with the absorbance of the PT complex. Figures 11 and 12 represent the spectrophotometric titration plots in which two straight lines were produced intercepting at a 1:1 ratio (HBA:HBD). Accordingly, one can conclude from Figures 9 to 12 that the PT complexes are formed based on a 1:1 ratio (HBA:HBD).

Optimization of Variables. Several important controlling factors in the process of proton transfer complex formation including the effect of reagent concentration, time, and temperature were studied, optimized, and evaluated in the following sections.

Effect of Reagent Concentration. The effect of reagent concentrations on the PT reaction was monitored by following the absorbance of $1.0 \cdot 10^{-4}$ mol·L^{-1} AZ with various amounts of each amine in MOH and MeCN. It has been found that maximum and constant absorbance was obtained with (1, 1.5, and 3) mL of pyrrolidine, propylamine, and triethylamine $1.0 \cdot 10^{-3}$ mol·L^{-1} in methanol, respectively. In acetonitrile, maximum absorbances of the PT complexes were obtained with (3 to 4) mL $5.0 \cdot 10^{-3}$ mol·L^{-1} of each amine.

Effect of Standing Time and Temperature. The effect of temperature was studied by following the absorbance of the PT complexes resulting by mixing $2.5 \cdot 10^{-4}$ mol·L^{-1} AZ with $2.5 \cdot 10^{-3}$ mol·L^{-1} from each amine in the range (15 to 40) °C. It has been found that 25 °C is the optimum temperature where the absorbance of the PT complexes recorded the highest and constant value. Moreover, the complexes were stable for more than four hours.

Analytical Data. Under the optimum experimental conditions, there was a linear relationship between absorbance of the PT complexes and AZ concentration in the range ($1.0 \cdot 10^{-5}$ to $1.0 \cdot 10^{-4}$) mol·L^{-1} in MeOH and ($1.0 \cdot 10^{-5}$ to $2.0 \cdot 10^{-4}$) mol·L^{-1} in MeCN with a correlation coefficient r (0.99) (Table 4). The regression equation and the molar absorbitivity (ε) were also calculated from the calibration graph applying the least-squares method (Table 4). The limits of detection (LOD) and quantification (LOQ) were calculated according to the IUPAC definitions.[31]The calculated values were listed in Table 4 for all the formed PT complexes. Generally, the LOD and LOQ recorded small values suggesting high accuracy of the method. It has been found also that the values of intercept a, slope b, confidence intervals of intercept α, and slope β recorded small values confirming excellent linearity between the absorbance and concentration.

The accuracy of the method was established by performing analysis of solutions containing 10 different amounts (within Beer's law limits) of AZ and measuring the absorbance of their PT complexes with each amine. The concentration of AZ was determined from the regression equation and then calculating the recovery percentages, the standard deviation S, and relative standard deviation RSD. The recovery percentage ranged from (99.80 to 100.80) with RSD ranging from 0.91 to 1.75 confirming high accuracy and precision of the analytical method (Table 5).

Comparison of the difference (between the determined value F and the true value Y) with the indeterminate error[32] $(\pm t_{n-1}S)/(\sqrt{n})$ was carried out, and the results were compiled in Table 5. It was found that $(Y - F)$ was less than $\pm tS/\sqrt{n}$ indicating that no significant difference existed between the mean and the true values.[32]

Hence, it can be concluded that the newly developed PT spectrophotometric method is highly sensitive, accurate, and rapid for analysis of AZ with different aliphatic amines in methanol and acetonitrile.

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