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Spectroscopic studies on the proton transfer reactions of 4-hydroxy-2-oxo-1, 2-dihydroquinolin-3-carbonitrile with different amines in acetonitrile

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ABSTRACT

Proton transfer reactions between 4-hydroxy-2-oxo-1,2-dihydroquinolin-3-carbonitrile (HQC) and propylamine (PA), triethylamine (TEA) and piperidine (Pip) have been studied spectro-photometrically in acetonitrile as a polar solvent. The molecular compositions of the formed complexes (I, II, and III) were determined using Job's and photometric titration methods. Minimum–maximum absorbances' method has been applied to estimate the formation constants of the formed complexes (K_{PT}). It has been found that K_{PT} reached higher value for HQC–TEA complex than PA and Pip ones. On the basis of the rapidity of the PT-reactions, a simple and accurate spectro-photometric method for determination of HQC was proposed. Beer's law was obeyed in the concentration range 0.19 to18.60 μg mL^{-1} with excellent correlation coefficients. The recovery percentages ranged from 99.63 to 99.99%. The solid complexes were synthesized and characterized using i.r., NMR spectroscopy and elemental analyses.

1. Introduction

Proton transfer is one of the most investigated chemical reactions in chemistry and biochemistry [1–4]. They play an important role in various chemical and biological processes like stabilizing biomolecular structures [5], controlling the speed of enzymatic reactions [6] as well as constructing supra-molecular structures [7]. Several physical properties of H-bonded complexes, e.g. excess of dipole moment (Δμ), change of ^{1}H, ^{13}C, ^{15}N chemical shifts (Δδ) and ^{35}Cl NQR frequency when plotted against ΔpKa (pKa ($B^{+}H$) − pKa (AH)), sigmoidal titration curves are obtained which were usually treated as evidence of the proton transfer equilibrium [8–11]. This equilibrium is strongly affected by the properties of the proton donor, proton acceptor and solvent polarity [12,13].

Functionalized quinolines are important constituents of pharmacologically active compounds, as these systems have displayed a broad spectrum of biological activities such as antiasthmatic [14], antibacterial [15], antifungal [16], antimalarial [17], antiviral [18], and anti-inflammatory [19] activities. In addition, quinolines are valuable precursors used for the synthesis of nano- and meso structures with enhanced electronic and photonic properties [20–22]. Of special interest, a series of new quinolin-3-carbonitrile derivatives have recently been synthesized reported to show significant activity as excellent selective cytotoxicity towards SMMC-772 cell line [23], antitumor [24], a novel type of EGFR inhibitor [25] and potent inhibitors of TP12 kinase [26]. Keeping in view the biological and pharmaceutical importance of the above mentioned quinolines and in continuation to our work on proton and electron transfer [10–12,27,28], herein we are gratified to report our results on the spectroscopic studies of the proton transfer reactions between 4-hydroxy-2-oxo-1,2-dihydroquinolin-3-carbonitrile (HQC) and different amines including propylamine (PA), piperidine (Pip) and triethylamine (TEA) in acetonitrile. In addition, we will study the molecular compositions of the formed complexes using Job's and photometric titration methods. Also, the formation constants of the complexes will be investigated and evaluated using the minimum–maximum absorbances' method. Furthermore, a sensitive spectroscopic method for estimating HQC has been chosen based on the fast production of the formed proton transfer complexes. The synthesis and characterization of the solid proton transfer complexes are important aims of this work.

2. Experimental

2.1. Materials, instrumentation and physical measurements

All chemical used were of analytical grade. Propylamine (PA), triethylamine (TEA) and pipridine (Pip) were supplied by Acros organic. Acetonitrile was supplied by Panreac.

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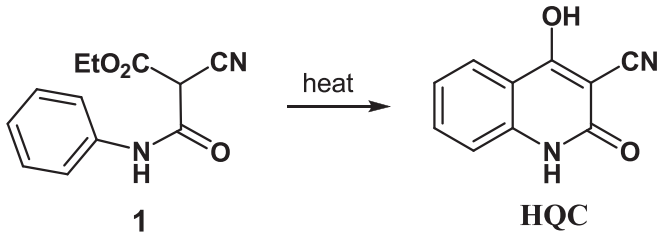


Scheme 1. Synthesis of HQC.

The electronic absorption spectra were recorded in the region (700 to 250) nm using UV–vis model Shimadzu UV-1601 with personal spectroscopy software version 3.7, connected to Shimadzu TCC-ZUOA temperature controller.

The infrared spectra of the prepared solid complexes were measured as KBr disks on Shimadzu FTIR-8400 S Fourier transform infrared spectrophotometer (Japan).

^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were measured on a Bruker DPX spectrometer using 10 mg of the sample in DMSO-d_6 (0.5 mL) as solvent and TMS as an internal standard; chemical shifts are expressed as δ ppm.

C, H and N contents were determined with the Micro Analyser, Perkin Elmer 2400 (USA).

2.2. Synthesis of HQC and the solid complexes

A suspension of ethyl 2-cyano-3-oxo-3-(phenylamino)-propanoat (**1**) [29] (2.60 g, 11.2 mmol) in 1,2-dichlorobenzene (40 mL) was refluxed for 1 h. After cooling to room temperature, the resulting solid product was collected by filtration, washed well with dioxane, dried and recrystallized from methanol to HQC (**2**) (Schemes 1) [29,30] as colorless crystals, yield (1.68 g, 81%); mp. 290–293 °C.

The solid 1:1 complexes of HQC with PA, TEA and Pip were synthesized by mixing equimolar amounts of both HQC and amine in acetonitrile and the resulting complex solutions were left standing overnight at room temperature. The solid complexes were separated as colorless crystals and dried over anhydrous calcium chloride for 24 h. The analytical data of the complexes (C, H, and N content) along with some of the physical properties are listed in Table 1.

2.3. Preparation of standard solutions of the proton donor and proton acceptor

Stock solutions of the proton donor (HQC, $1.0\cdot10^{-3}$ mol L^{-1}) and the proton acceptors (PA, TEA and Pip, $1.0\cdot10^{-3}$ mol L^{-1}) were freshly prepared before each series of measurements by dissolving precisely weighed amounts in the appropriate volume of acetonitrile. Solutions for spectroscopic measurements were made by mixing appropriate volumes of stock donor and acceptors solutions and pure solvent.

2.4. Determination of the formation constants of the complexes (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 HQC in acetonitrile ($1.0\cdot10^{-3}$ mol L^{-1}) was transferred into a series of 10 mL calibrated flasks. To each of these were added different concentrations of freshly prepared stock amines solutions ($1.0\cdot10^{-3}$ mol L^{-1}) and diluted to the mark with acetonitrile. The absorbance of the mixture solutions was recorded against a solvent blank. The lowest amine concentration led to the minimum absorbance of the complex ($A_{min.}$). The concentration of the amine was increased gradually and the absorbance was recorded at the maximum absorption band of the complex ($A_{mix.}$) until the highest and constant absorbance of the formed complex was obtained ($A_{max.}$). The complex formation constants (K_{PT}) were estimated as given by the following equation [12,27,28,31].

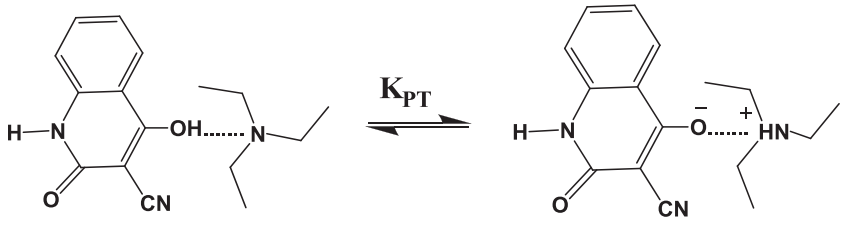
$$A_{max.} = A_{mix.} + \frac{A_{mix.} - A_{min.}}{K_{PT}\cdot C_{amine}} \quad (2)$$

where $A_{max.}$ and $A_{min.}$ are the maximum and minimum absorbances of the proton transfer complex. $A_{mix.}$ is the complex absorbance between $A_{max.}$ and $A_{min.}$ 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.

3. Results and discussion

3.1. Electronic spectra

The electronic spectra of $1.0\cdot10^{-4}$ mol L^{-1} HQC and the proton transfer complexes resulting from mixing $1.0\cdot10^{-4}$ mol L^{-1} HQC



Molecular complex **Hydrogen-bonded ion pair**

Scheme 2. Proton transfer equilibrium.

Table 1
Elemental analyses, stoichiometry, melting point and color of complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip.

Complex	Expected			Found			Stoichiometry	mp (°C)	Color
	%C	%H	%N	%C	%H	%N			
I	63.15	6.88	17.00	62.98	6.91	16.88	1:1	227–229	Colorless
II	66.44	7.96	14.53	66.11	8.03	14.43	1:1	141–143	Colorless
III	66.35	6.27	15.48	66.29	7.71	15.14	1:1	235–236	Colorless

with $1.0\cdot10^{-4}$ mol L^{-1} of each amine in acetonitrile are presented in Fig. 1 at room temperature. The formed complexes showed an absorption bands near 308 nm which could be assigned to $\pi\rightarrow\pi^*$ of the formed complexes. Fig. 2 shows the effect of amine concentration on the formation of the complexes through mixing $1.0\cdot10^{-4}$ mol L^{-1} HQC with various concentrations of each amine. It has been found that, the increase in the amine concentration led to increase the absorption of the complex band and the decrease of HQC band intensities at 291 and 353 cm^{-1} respectively, until complete disappearance at 1:1 molar ratio of amine with HQC. This confirms the shift of the prototropic equilibrium to the hydrogen bonded ion pair O…H^+N (Scheme 2). It is also observed in Fig. 2, the appearance of an isosbestic point at 330 nm confirming the existence of prototropic equilibrium between HCQ and the amine.

3.2. Formation constants of the complexes (K_{PT})

Based on the electronic spectra of the formed complexes at various concentrations of the amines, K_{PT} were estimated by using the minimum–maximum absorbances' method, the results are collected in

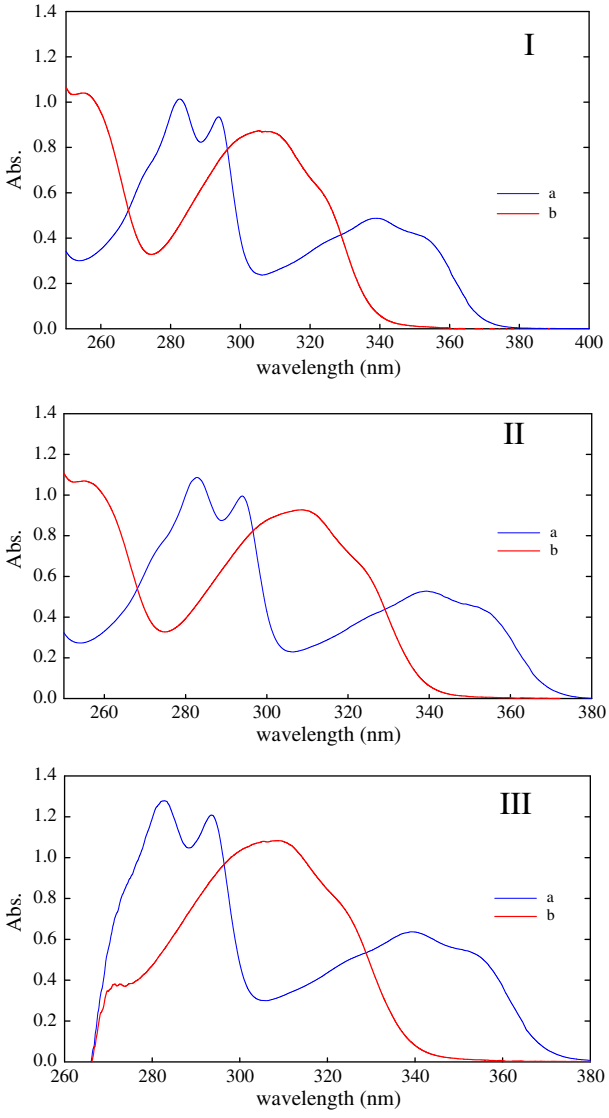


Fig. 1. Electronic spectra : (I) a–$1\cdot10^{-4}$ mol L^{-1} HQC and b–$1\cdot10^{-4}$ mol L^{-1} HQC + $1\cdot10^{-4}$ mol L^{-1} PA, (II) a–$1\cdot10^{-4}$ mol L^{-1} HQC, b–$1\cdot10^{-4}$ mol L^{-1} HQC + $1\cdot10^{-4}$ mol L^{-1} TEA and (III) a–$1\cdot10^{-4}$ mol L^{-1} HQC, b–$1\cdot10^{-4}$ mol L^{-1} HQC + $1\cdot10^{-4}$ mol L^{-1} Pip, all in acetonitrile.

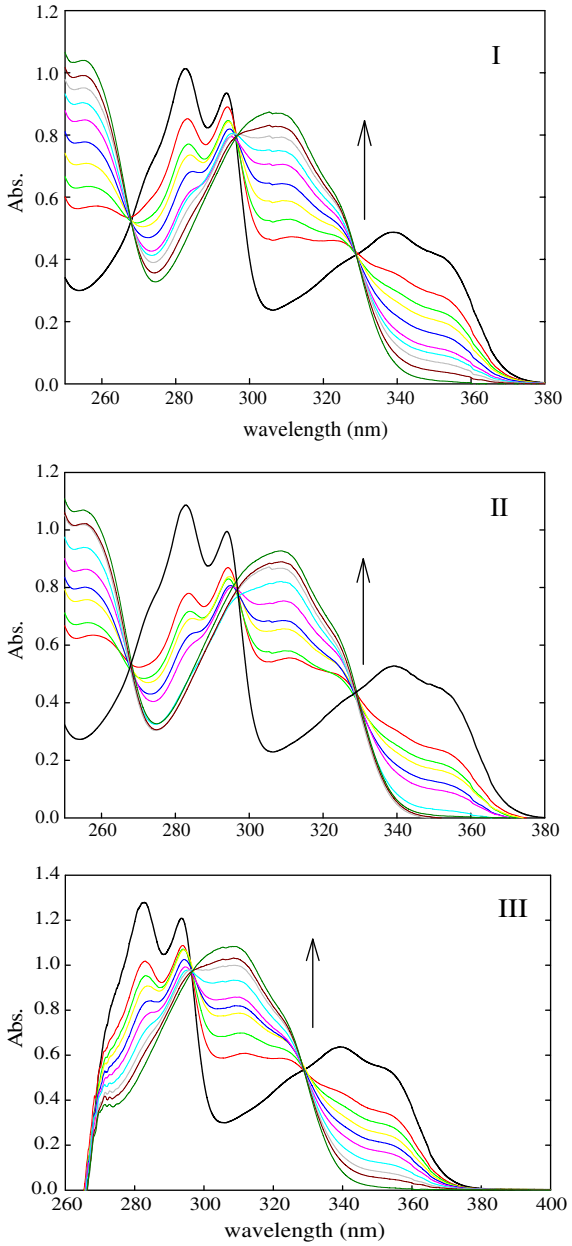


Fig. 2. Electronic spectra of complexes in acetonitrile between $1\cdot10^{-4}$ mol L^{-1} HQC and I–(1) 0.0, (2) $3.0\cdot10^{-5}$, (3) $4.0\cdot10^{-5}$, (4) $4.5\cdot10^{-5}$, (5) $5.5\cdot10^{-5}$, (6) $6.5\cdot10^{-5}$, (7) $7.0\cdot10^{-5}$, (8) $7.5\cdot10^{-5}$, (9) $8.0\cdot10^{-5}$, (10) $1\cdot10^{-4}$ mol L^{-1} PA, II–(1) 0.0, (2) $3.0\cdot10^{-5}$, (3) $3.5\cdot10^{-5}$, (4) $4.0\,10^{-5}$, (5) $4.5\cdot10^{-5}$, (6) $5.0\cdot10^{-5}$, (7) $6.0\cdot10^{-5}$, (8) $6.5\cdot10^{-5}$, (9) $8.0\cdot10^{-5}$, (10) $1\cdot10^{-4}$ mol L^{-1} TEA and III–(1) 0.0, (2) $3\cdot10^{-5}$, (3) $4\cdot10^{-5}$, (4) $5\cdot10^{-5}$, (5) $5.5\cdot10^{-5}$, (6) $6\cdot10^{-5}$, (7) $7\cdot10^{-5}$, (8) $7.5\cdot10^{-5}$, (9) $8\cdot10^{-5}$, (10) $1\cdot10^{-4}$ mol L^{-1} Pip.

Tables 2 and 3. Generally, K_{PT} recorded high values suggesting the formation of stable complexes. One observes in Table 3, that K_{PT} depends on the structure of the studied amines where K_{PT} recorded the highest value for HQC–TEA complex than the other two amines. This result could be interpreted based on the high electron density on the nitrogen

Table 2
Minimum, maximum and mixture concentrations (mol L^{-1}) of the added amines at 25 °C.

Complex	C_{min}	$C_{max}\cdot10^5$	$C_{max}\cdot10^5$							
I	0.0	10	3.0	4.0	4.5	5.5	6.5	7.0	7.5	8.0
II	0.0	10	3.0	3.5	4.0	4.5	5.0	6.0	6.5	8.0
III	0.0	10	3.0	4.0	5.0	5.5	6.0	7.0	7.5	8.0

Table 3
Minimum–maximum absorbance's data and formation constants at 25 °C.

Complex	λ_{max} nm	A_{min}	A_{max}	A_{mix}								$K_{PT} \cdot 10^{-3}$ (L mol^{-1})
I	308.5	0.245	0.870	0.468	0.526	0.588	0.643	0.706	0.749	0.793	0.827	58.2
II	308.5	0.237	0.928	0.556	0.580	0.657	0.685	0.754	0.821	0.867	0.890	82.6
III	308.0	0.317	1.083	0.600	0.696	0.787	0.820	0.853	0.932	1.000	1.030	60.9

center of TEA from the high inductive effect of the three ethyl groups. Although piperidine has higher pKa, 11.1, than TEA, 10.65, HQC–Pip complex recorded lower K_{PT} value than HQC–TEA one. The situation could be rationalized based on the formation of intermolecular hydrogen bonding between acetonitrile and piperidine molecules which increases the steric hindrance and lowers the K_{PT} value. It is also observed in Table 3 that HQC–PA complex recorded the least K_{PT} value concordance with its lower pKa, 9.33 together with the formation of intermolecular hydrogen bonding with acetonitrile molecules.

3.3. Composition of the proton transfer complexes

The compositions of the formed complexes were determined by applying Job's method of continuous variations [32] and photometric titrations. Fig. 3 represents the continuous variation method plots according to Job's method, the maximum absorbance was recorded at 0.5 mole fraction indicating 1:1 complex formation (proton donor: proton acceptor). Photometric titrations at (308 to 309) nm for the reaction between the studied proton donor HQC and amines in acetonitrile were carried out as follows: the concentration of HQC was kept constant at $1.0 \cdot 10^{-3}$ mol L^{-1}, whereas that of the acceptor amines was changed over the wide range from $1.0 \cdot 10^{-4}$ to $1.5 \cdot 10^{-3}$ mol L^{-1}. The proton acceptor:proton donor molar ratio obtained in this case varied (from 0.1 to 1.5). Fig. 4 represents the photometric titration plots where two straight lines were produced intercepting at 1:1 molar ratio.

3.4. 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 as follow. The effect of reagent concentrations on the complex reaction was monitored by following the absorbance of 1 mL $1.0 \cdot 10^{-3}$ mol L^{-1} HQC with various amounts of each amine in acetonitrile. It has been found that maximum and constant absorbance was obtained with 1.0 mL of $1.0 \cdot 10^{-3}$ mol L^{-1} of each amine. The effect of temperature was studied by following the absorbance of the complexes resulting

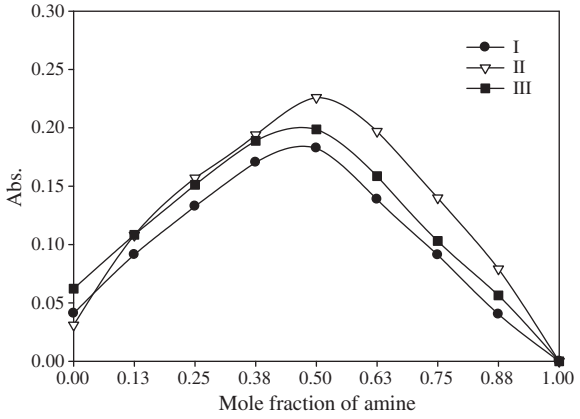


Fig. 3. Job's plots of 1:1 complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip in acetonitrile.

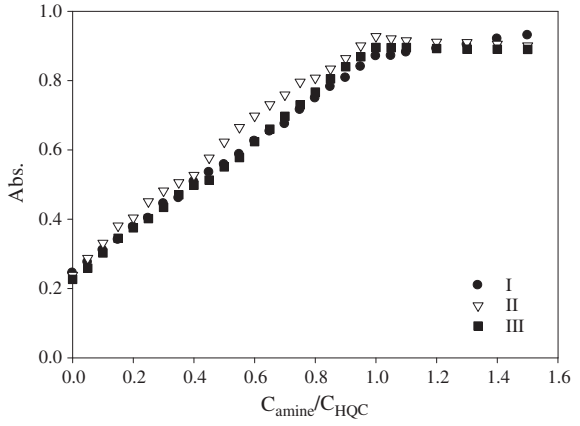


Fig. 4. Photometric titration plots of 1:1 complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip in acetonitrile.

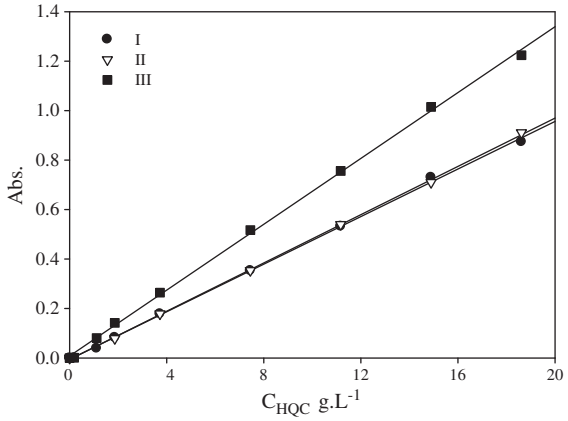


Fig. 5. Beer's law plots of 1:1 complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip in acetonitrile.

Table 4
Quantification parameters of complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip.

Parameter	Complex		
	I	II	III
Beer's law limits, μg mL^{-1}	0.19–18.60	0.19–18.60	0.19–18.60
Limit of detection, μg mL^{-1}	0.70	0.68	1.30
Limit of quantification, μg mL^{-1}	2.30	1.66	6.30
Molar absorptivity ε, L mol^{-1} mL^{-1}	8974	9084	12356
Intercept, a	−0.0067 ± 0.0060	−0.0062 ± 0.0037	0.0104 ± 0.0085
Slope, b	0. 0482 ± 0.0006	0.0488 ± 0.0003	0.0664 ± 0.0009
Correlation coefficient, r	0.9990	0.9996	0.9990

Table 5
Evaluation of accuracy and precision of the method.

Complex	Rec. (%)	*S*	RSD,%	|F–Y|	$\pm\frac{ts}{\sqrt{n}}$	Confidence limits
I	99.63	0.647	0.650	0.0153	±0.560	99.63 ± 0.560
II	99.84	0.510	0.511	0.0135	±0.441	99.84 ± 0.441
III	99.99	0.800	0.803	0.0514	±0.691	99.99 ± 0.691

F = amount taken; Y = amount found from regression equation.
t = 2.447 for n = 8 at 95% confidence level.
RSD = relative standard deviation, *S* = standard deviation.

by mixing $1.0\cdot10^{-4}$ mol L^{-1} HQC with $1.0\cdot10^{-4}$ mol L^{-1} from each amine in the range 15–40 °C. It has been found that 15 °C is the optimum temperature where the absorbance of the complexes recorded the highest and constant value. Moreover, the complexes were stable for more than 3 h.

3.5. Analytical data

Under the optimum experimental conditions, there was a linear relationship between absorbance of the complexes and HQC concentration in the range (0.19 to18.60 μg mL^{-1}) with a correlation coefficient (r) (0.99) (Fig. 5).The regression equations were calculated from the calibration graph applying the least squares method. They were A = 0.0482 C − 0.0067 for HQC–PA complex, A = 0.0488 C − 0.0062 for HQC–TEA complex and A = 0.0664 C + 0.0104 for HQC–Pip complex where A is the absorbance of the complex and C is the concentration of HQC in μg mL^{-1}. The limits of detection (LOD) and limits of quantification (LOQ) were calculated according to the IUPAC definitions [33]. The calculated values were listed in Table 4 for all of the formed complexes. Generally, the LOD and LOQ recorded small values, suggesting high sensitivity of the method. Also, it has been found that the values of intercept, slope, confidence intervals of intercept and slope recorded

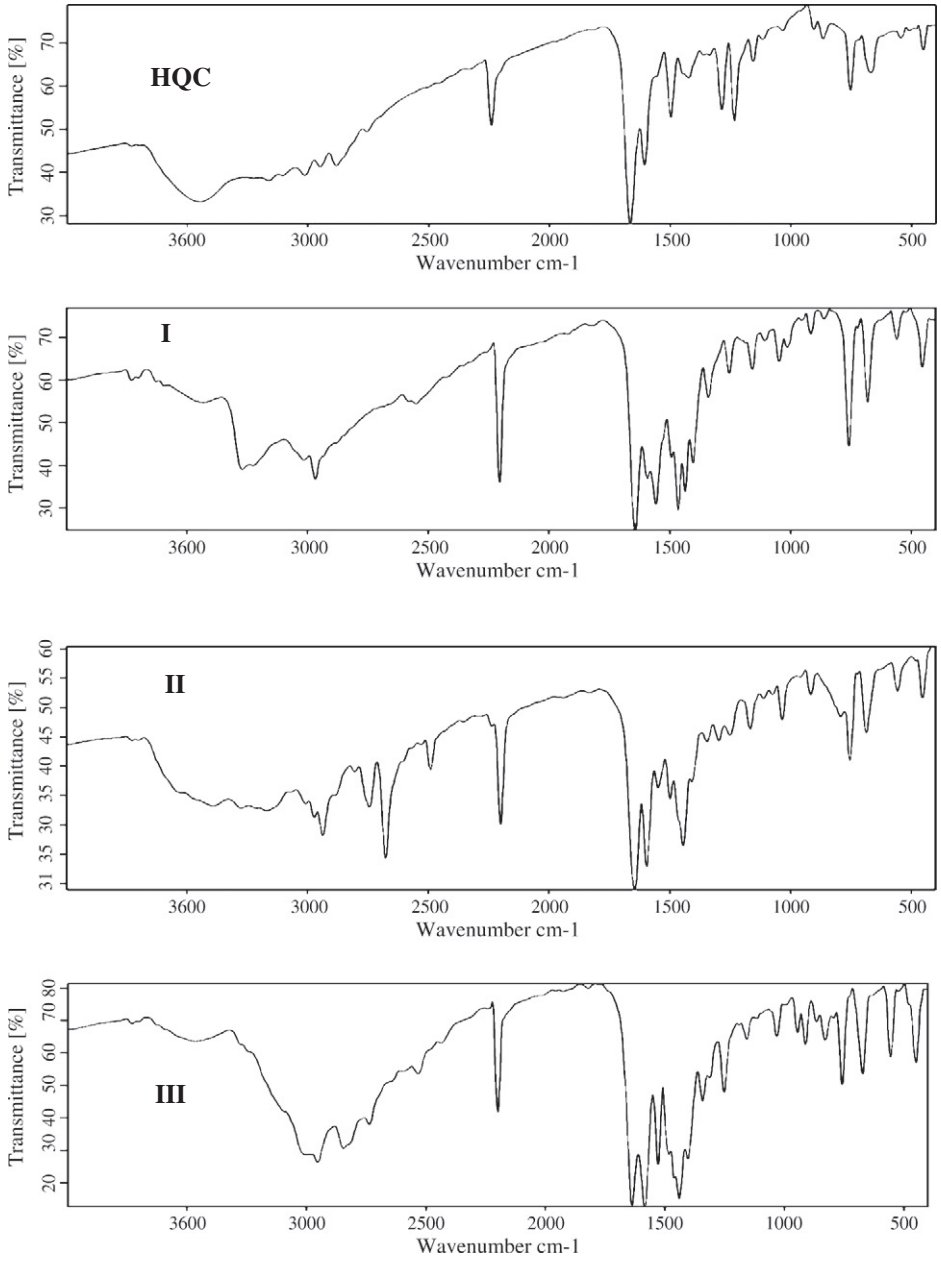


Fig. 6. FTIR spectra of HQC and its complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip in the range 4000–400 cm^{-1}.

small values confirming excellent linearity between the absorbance and concentration.

The accuracy of the method was established by performing analysis of solutions containing 8 different amounts (within Beer's law limits) of HQC and measuring the absorbance of its complexes with each amine. The concentration of HQC was determined from the regression equation and then calculating the recovery percentages, standard deviation S and relative standard deviation RSD. The recovery percentage ranged from 99.63 to 99.99 with RSD<1%, 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 [34] 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 [34]. Hence, it can be concluded that the newly developed spectrophotometric method is highly sensitive, accurate and rapid for analysis of HQC with different amines in acetonitrile.

3.6. Characterization of the formed complexes

3.6.1. FTIR spectra

The formation of 1:1 complexes between HQC and the different amines was ascertained from a comparison of the i.r. spectra of complex with that of reactants. The FTIR spectrum of HQC was presented in Fig. 6 where a broad band was recorded at 3442 cm^{-1} attributing to

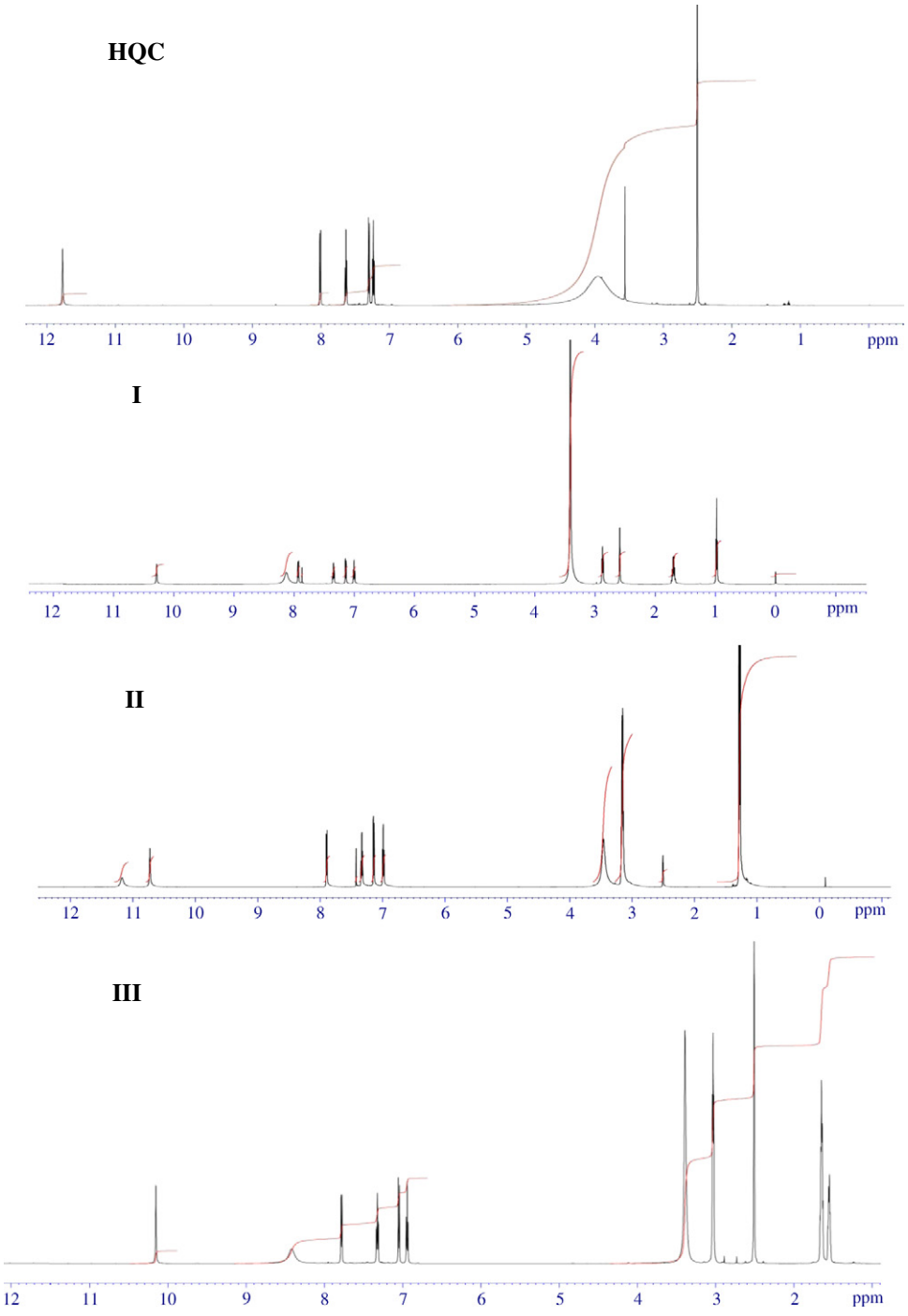


Fig. 7. ^{1}H NMR spectra of HQC and its complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip.

hydrogen bonded OH of HQC with the neighboring cyano group. The situation was confirmed from the lower intensity of ν (CN) at 2241 cm^{-1} than those of the proton transfer complexes (Fig. 6). The i.r. spectrum of HQC–PA complex (I) was presented in Fig. 6 where the OH band of HQC was disappeared and the asymmetric and symmetric stretching vibrations of the amino group (NH_2) of propylamine were strongly disturbed at 3270 cm^{-1}. This confirms the transfer of HQC proton to the amino group of propylamine to form the complex. Another evidence for the formation of the complex HQC–PA is coming from the shifts of its ν (CN) and ν (C=O) bands to 2204 and 1644 cm^{-1} compared with 2241 and 1664 cm^{-1} for HQC alone. The formation of the complex (II) is proved from the disturbance of the OH stretching region in the range 3000–3500 cm^{-1} together with the appearance of ν (N^+H) at 2741 cm^{-1} (Fig. 6). Furthermore ν (CN) and ν (C=O) bands of the complex are shifted to 2200 and 1645 cm^{-1} compared with 2241 and 1664 cm^{-1} for HQC itself. Concerning the i.r. spectrum of the complex (III) (Fig. 6), a new vibrational band was appeared at 2736 cm^{-1} attributing to ν (N^+H) and confirming the migration of HQC proton towards the piperidine ring nitrogen to form the hydrogen bond ion pair $O^-...H^+N$. Also, the shifts of ν (CN) and ν (C=O) bands

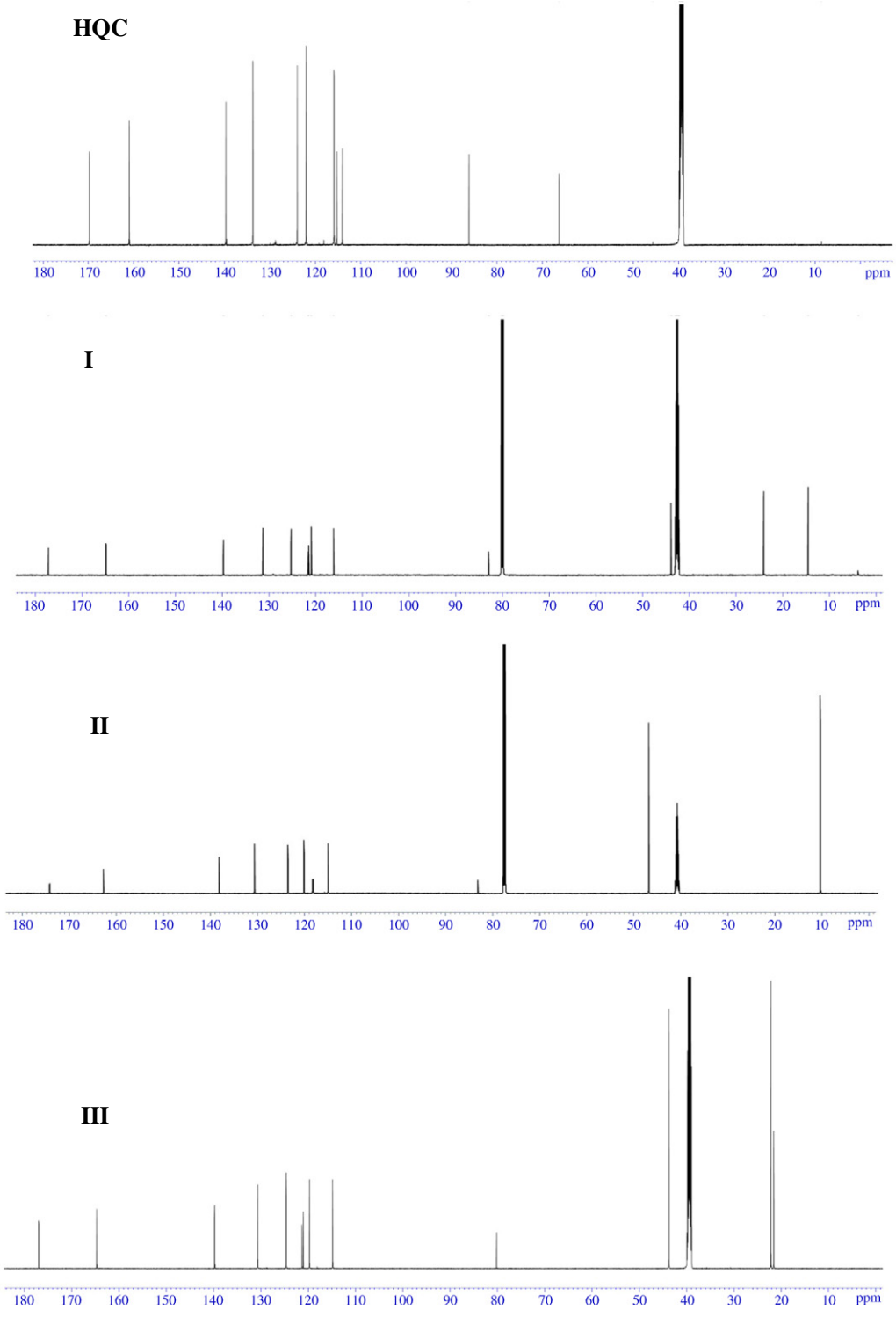


Fig. 8. ^{13}C NMR spectra of HQC and its complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip.

Table 6
^{1}H and ^{13}C NMR chemical shifts (ppm) of HQC and its complexes: (I) HQC–PA, (II) HQC–TEA and (III) HQC–Pip.

		^{1}H NMR		
H and C atoms	HQC	I	II	III
OH	3.95	–	–	–
H(5)	7.3	7.14	7.46	7.05
H(6)	7.24	7.00	6.99	6.95
H(7)	7.64	7.34	7.33	7.32
H(8)	8.01	7.92	7.89	7.78
Quin. NH	11.8	10.28	10.73	10.15
NH^{+}	–	8.13	11.17	8.40
CH_3 amine	–	0.98	1.27	–
CH_2 amine	–	1.69, 2.87	3.15	1.55, 1.68, 3.05
		^{13}C NMR		
C (3)	86.18	81.23	82.89	80.20
CN	114.06	115.34	115.48	114.80
C(8)	115.27	120.25	118.72	119.70
C(4a)	115.91	120.81	118.88	121.01
C(5)	122.16	120.92	120.71	121.28
C(6)	124.82	127.72	124.2	124.62
C(7)	133.69	130.9	131.50	130.63
C(8a)	139.83	139.60	139.19	139.69
C(4)	160.88	165.40	164.36	164.67
C=O	169.71	178.09	176.07	176.94
CH_3 amine	–	10.97	8.38	-
CH_2 amine	–	20.73, 41.13	45.71	21.58, 22.17, 43.74

of the complex to 2199 and 16384 cm^{-1} compared with 2241 and 1664 cm^{-1} for HQC are further proofs for the formation of the complex (III). Important observations from Fig. 6 are the appearance of broad absorptions down 1600 cm^{-1} with ν (H) lies at 1218, 1212 and 1223 cm^{-1} which confirms the formation of the complexes I, II and III [10].

3.6.2. ^{1}H and ^{13}C NMR spectra

The ^{1}H and ^{13}C NMR spectra of HQC and its complexes are shown in Figs. 7 and 8 and the resonance signals are compiled in Table 6. The ^{1}H NMR spectrum of HQC showed resonance signal at 3.95 ppm assignable to the OH proton. This resonance signal was disappeared in the spectra of the complexes, instead a resonance signal appeared at $\delta = 8.13$ ppm in the spectra of the complex (I) assignable to $N^{+}H_3$ protons. This confirms the migration of the OH proton towards the amino group of propylamine to form the complex. The ^{1}H NMR spectrum of complex (II) displayed a resonance signal at $\delta = 11.17$ ppm which could be attributed to the formation of the proton transfer complex $O-H^{-}-N^{+}-(Et)_3$. Concerning complex (III), a resonance signal at $\delta = 8.4$ ppm was observed attributing to $N^{+}H$ confirming the proton transfer towards the piperidine ring nitrogen to form the complex. The observed resonance signals of the reactants in ^{1}H NMR spectra of the formed complexes except the OH proton suggest their formation. An important finding from Table 6 is the appearance of NH resonance signal of the quinoline ring in the complexes at high field (lower δ values) compared with the resonance signal of NH of HQC alone which appeared at down field (high δ value). The situation could be interpreted based on the proton transfer from HQC to amines which changes the charge distribution in the complexes compared with the reactants.

The ^{13}C NMR spectra of HQC and its complexes (I, II and III) are shown in Fig. 8. One observes that the spectra of the complexes included the resonance signals of both HQC and amines confirming their formation. An important observation from Table 6 is the appearance of the resonance signal of the carbonyl carbon in the complexes at down field (high δ value) compared with the resonance signal of the carbonyl carbon of HQC alone which appeared at high field (low δ value). This could be interpreted based on the increase of charge density on the carbonyl carbon, as a result of proton transfer complex formation.

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