ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

Tuning Fluorescence Properties of 2, 2′- biquinoline Using Metal Cation

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By

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A project submitted to the School of Graduate Studies in partial fulfillment of the Requirement for the Degree of Master of Science in Chemistry

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Approved **Signature**

Dr. Ahmed Mustefa **----------**

(Examiner)

Declaration

This project is my original work, has not been presented for a degree in this and other university and all resources and materials used for this project have been duly acknowledged.

Name: TEWODROS BEZABIH BIRHANU

Signature _____

The project has been submitted for examination with my approval as project advisor.

Name Signature

Place and date of submission:

School of Graduate Studies

Addis Ababa University

2011

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I would like to thank my advisor Dr. Mesfin Redi for his genuine cooperation and guidance throughout my project work.

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Acronyms and abbreviations

INDO	intermediate neglect of differential overlap
DFT	Density Functional Theory
B3LYP	Becke, three-parameter, Lee-Yang-Parr
STO-3G	Slater-Type Orbital approximated by 3 Gaussians
UV-Vis	Ultraviolet-Visible

Abstract

The steady state absorption, fluorescence excitation and emission spectra of 2, 2′- biquinoline have been studied in polar and non-polar solvents. Absorption spectra are almost independent of solvent polarity. The dependence of fluorescence emission on excitation wavelength was observed in acetonitrile, dichloromethane and p-dioxane but independent of excitation energy in cyclohexane. Addition of metal ion and varying pH of the solution shifted the absorption and excitation band to the red-edge. Corresponding excitation bands of the metal free conformers were compared to the stable conformers of metal-chelated and protonated 2,2′- biquinoline. Study of the rotational profile of 2, 2′- biquinoline at semi-empirical of INDO methods shows two energy minima corresponding to two conformations of different energy, cis/trans structures, with barrier to rotation comparable for trans to the room temperature thermal energy but less for cis conformer. It is shown that distributions of energetically different conformers of the molecule (cis/trans) in the ground state are responsible for the dual fluorescence behavior of the systems.

1 Introduction

Spectroscopy is an emerging technology with potential applications, for basic research in these filed the understanding of various photophysical and photochemical processes are essential. The past two decades have witnessed the emergence of fluorescence and phosphoresence to become among the most useful of tools in experimental biology and chemistry. The presence of electron donor and acceptor groups on opposite sides of the molecule, connected by a highly delocalized electron system, is very important to their nonlinear optical properties. The luminescing molecules' of interest to this group are often extremely complicated drugs and metabolism which do not lend themselves to detailed understanding by rigorous quantum mechanical treatments[1].

The exploration for the diagnosis of dual fluorescence of organic system has been very rapid in the recent years[2-5], The molecule 4-(Dimethylamino)benzonitrile (DMABN) has over the years become the favorite example of a dual fluorescent molecule[2-4]. Since the discovery that this molecule emits from two different intramolecular singlet excited states[5], a locally excited state LE and a charge transfer state CT. The original hypothesis put forward by Lippert in 1959 was based on a solvent polarity induced reversal of the two directly populated lowest excited states S_1 and S_2. Although it was pointed out that a small energy gap was essential for the appearance of the dual emission, the molecular configuration of the two emitting states was not discussed[3]. On the other-hand, hetroatomic organic molecule that have different conformation that attributed to its tendency to exist in cis/trans forms in equilibrium expected will have dual emission bands from the different conformation forms both in the ground and in excited states. The rotation of the more flexible part of a bichromophoric molecule acts as a main fluorescence quencher of the system[6]. Presence of free rotation about a sigma bond between chromophores leads to the adoption of several different three-dimensional shapes called conformations[7]. Because each of the various conformations of a molecule has different properties, the conformation the molecule normally adopts has a profound influence on its physical and chemical properties. 2, 2′- biquinoline has electronic structure similar to those groups of compounds, which have been proved to have the above-mentioned properties. Attributed to its tendency to exist in cis/transforms in equilibrium, 2, 2′- biquinoline is expected to have dual emission bands from the different conformation forms both in the ground and in excited states.

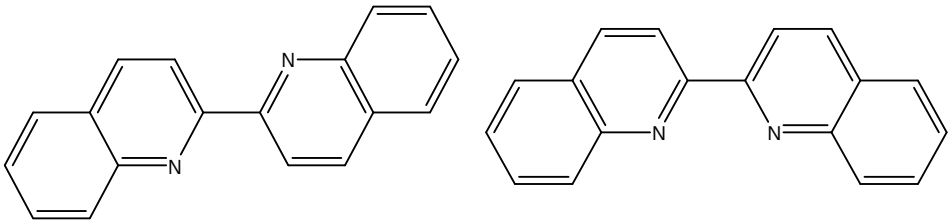
1.1 Literature Review

The 2, 2′- biquinoline solution absorption spectrum shows distinct band positions in 225-350 nm region having 0-0 band at around 340 nm and a prominent high energy band at 261 nm along with the vibrational band at around 329 nm. In addition, there is a weak hump at around 237 nm. The fluorescence spectrum of pure 2, 2′- biquinoline solution shows a broad and intense band profile in the 325-450 nm region. This broad band actually consists of several diffused overlapping vibrational bands with 0-0 band at around 368 nm. The large shift of 0-0 band in fluorescence spectrum in comparison to the solution absorption spectrum may be due to the deformation produced in the electronic states of the molecule[8]. The microcrystal fluorescence spectrum shows prominent and intense 0-0 band at 396 nm along with the weak hump at 441 nm and an almost indistinguishable hump at around 417 nm. The high-energy band at 368 nm in solution spectrum is totally absent in microcrystal spectrum. The total quenching of this high-energy band is due to the reabsorption effect arising due to the formation of microcrystalline aggregates and have been observed in several other molecules[9].

2, 2′- biquinoline and its derivatives are widely used in various thin film application devices owing to their strong photoluminescence and electroluminescence properties[10]. The biquinoline-dicarboxy bridge introduced in the dual host can act as a positive binding site for host-guest complexation and as a versatile coordinating site for metal ions[11]. The Zn^{2+} ion has been widely used in hybrid frameworks due to its versatile coordination numbers and geometries and its d^{10} configuration used in spectral. The change in geometry results when 2, 2′-biquinoline and other azaaromatics coordinate with metal ions like Zn^{2+} changes the photophysical pro-perties of the ligand[12]. A red shifted absorbance spectrum has been observed for the Zn^{+2} co-mplexes with 2, 2′- biquinoline, the rich coordination modes of the ligan 2, 2′- biquinoline a 2Dmetal-organic framework has been obtained , providing an unprecedented coordination mode. It exhibits a 2D zig-zag network assisted by face-to-face π -π interactions between quinoline rings[13]. Moreover, 2, 2′-biquinoline is widely used as the parent compound to make drugs especially anti-malarial medicines, fungicides, biocides, alkalod, dyes[14].

Although all molecules are capable of absorption, fluorescence is not observed in large number of compounds. Fluorescence is generally observed in those organic molecules that have rigid framework and not many loosely coupled substituent's through which vibronic energy can flow out. From structural point of view, 2,2′-biquinoline presents two important features that reflect its elusive photophysical properties. The first one is the presence of relatively close-lying n→π* and π→π* excited states which can be coupled vibronically out-of-plane vibrations with subsequent modification of the potential energy surface and mixed spectral and photophysical properties. It is well known that the solvent plays an important role in this effect by influencing the energy gap between the states involved. The second important feature is the presence of a single bond connecting two azaaromatic moieties, with the possibility of rotation of the rings to reach the minimum-energy conformation with relatively small barriers to be overcome. Related to this feature is the presence of rotamers (rotational isomers) with different possible spectral and photophysical properties. The presence of rotational isomers has recently been evidenced for many ethylene-substituted molecules [15].

Due to more stability of the trans form (i), there are little information on the properties of the metal-free cis conformer (ii). Here in this study, of organized molecular assemblies of mother chromopher of the report of the detailed, spectroscopic characterizations of 2, 2′- biquinoline in the light of UV-V's absorption, steady state fluorescence spectroscopic study and theoretically using computational methods. The ultimate goal of this work is therefore, to investigate the existence of the ground state cis conformer and its fluorescence properties in polar solvents.



(i) (ii)

Scheme 1: TRANS (i) and CIS (ii) conformer of 2, 2′- biquinoline

1.2 OPTICAL ABSORBTION

Spectra in the visible and ultraviolet regions arise from transitions between different energy levels of electrons in atoms or molecules. Absorption spectra are graphs of intensity of absorbed radiation versus the wavelength of radiation. The spectra from the near infrared to the ultraviolet are sometimes called optical spectra, the spectra of atoms consist of sharp line, and those of molecules' appear to consist of bands, in which a densely packed line structure is often revealed with spectrographs of high resolving power, i.e., capable of separating small differences in frequency. Transition between different electronic levels gives rise to spectra in the visible or ultraviolet region, called electronic spectra. Transition between vibrational levels within the same electronic state are responsible for spectra in the near infrared (<20nm), called vibration-rotation spectra. Finally, spectra are observed in the far infrared (>20nm), arising from transitions between rotational levels belonging to the same vibrational level; these are called pure rotation or microwave spectra[6].

Absorption of Polyatomic Molecules

The orbital's for the ground sate of molecules are usually either σ or π type. Excited ant bonding orbital of σ and π types are denoted σ* and π* orbital. There are also orbital's that lone pair of electrons on hetro-atoms such as N or O. This are nonbonding orbital's, designated as n orbital's. Usually, they are occupied orbital's of highest electrons energy and hence are particularly important in electronic spectra.

In absorption spectroscopy, tow important type of orbital's are considered: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Both of these refer to the ground state of the molecule. Energetically favored electron will be from HOMO to LUMO. The energy of the electron transitions is generally in the following order;[16]
$n\rightarrow \pi^* < \pi\rightarrow\pi^* < n\rightarrow\sigma^* < \sigma\rightarrow\pi^* < \sigma\rightarrow\sigma^*$

Electronic promotions to n→π* states are possible when heteroatom's are incorporated into a molecule. In general, low-energy n→π* transitions are observed when the heteroatom is conjugate to a π-electron system, but still has lone-pair electrons. Examples include aromatic compounds' containing carbonyl-, azo-, nitroso-, and nitro groups. The n→π* transitions can

open up additional nonradiative electronic relaxation channels that can dramatically affect the excited-state daynamics of a heteroatom molecule relative to the heteroatom-free hydrocarbon counterpart[17].

Absorption of light

Absorbance spectroscopy is a widely used analytical technique. At its very core, this method involves comparing the light transmitted through a blank to the light transmitted through an absorbing species. If the incident light (at a specific wavelength, l) has intensity I_0, and it passes through a sample that absorbs at the wavelength l, the light intensity, I, leaving the sample is attenuated. These two quantities are related by the molar extinction coefficient at the wavelength of interest, ε, the concentration of the absorbing species, C, and the length of the path that the light traverses through the sample, l.

$$I = I_o e^{-\varepsilon Cl}$$

This is a form of Beer's Law, and by manipulating the equation, the following form can be

achieved.

$$-\log\left(I / I_o\right) = \varepsilon Cl$$

The quantity that was measured in absorption spectroscopy is the logarithmic term, which is

Commonly called the absorbance. By substituting in A for the log term, we arrive at the

Common form of Beer's Law.

$$A = \varepsilon Cl$$

Where A is the absorbance of the sample in the beam. The ratio of the light intensity transmitted by the sample to the light intensity incident on the sample is the transmittance T

$T = I/I_o$ and $A = -\log T$

Transmittance will be expressed as a percentage, i.e. $T = 100\ I/I_o$ [6]

The Franck-Condon principle

According to the Born-Oppenheimer approximation, the motions of electrons are much more rapid than those of the nuclei (i.e. the molecular vibrations). Promotion of an electron to an anti-bonding molecular orbital upon excitation takes about 10^{-15} sec, which is very quick compared to the characteristic time for molecular vibrations (10^{-10}-10^{-12}sec). This observation is the basis of the Franck-Condon principle: an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition is called vertical transition[16]

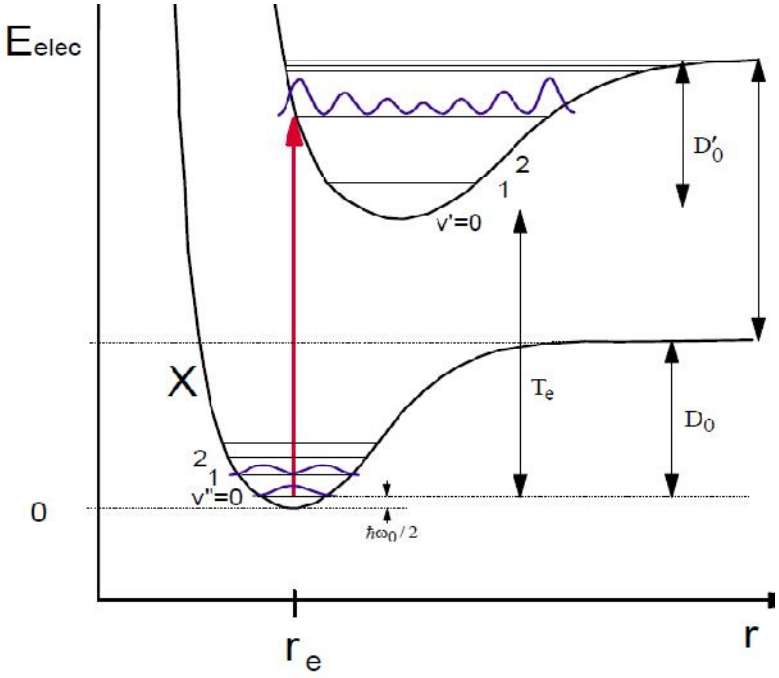


Figure 1: vertical transition permitted by the franck-condon principle between two electronic state of diatomic X. The dissociation energies of ground and excited electronic state are D_0 and D_0' respectively. ΔE (atomic) is the difference in energy between the separated atoms arising from the tow stats and T_e, is the difference in energy between the two electronic states.

Isosbestic Points

In spectroscopy, an isosbestic point is a specific wavelength at which two chemical species have the same molar absorptive (ε) or more generally are linearly related. This occurs because the two substances absorb light of that specific wavelength to the same extent, and the analytical concentration remains constant. Isosbestic points are commonly met when electronic spectra are taken (a) on a solution in which a chemical reaction is in progress (in which case the two absorbing components concerned are a reactant and a product, A + B), or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g., an acid-base indicator equilibrium. The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. A pair of substances can have several isosbestic points in their spectra. When a 1-to-1 (one mole of reactant gives one mole of product) chemical reaction (including equilibria) involves a pair of substances with an isosbestic point, the absorbance of the reaction mixture at this wavelength remains invariant, rega-rdless of the extent of reaction (or the position of the chemical equilibrium). The requirement for an isosbestic point to occur is that the two species involved are related linearly by stoichiometry, such that the absorbance is invariant for one particular wavelength. Thus other ratios than one to one are possible. The presence of an isosbestic point typically does indicate that only two species that vary in concentration contribute to the absorption around the isosbestic point[16].

1.2.1 Factors affecting Absorption Spectra

Solvent effect on Absorption spectra

When absorption are measured in solvents of different polarity, it is found that the positions, intensity, and shape of the absorption bands are usually modified by the solvent[18]. These changes are a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-induced dipole, hydrogen bonding, etc.) which above all tend to alter the energy different between ground and excited state of the absorbing species containing the chromophore.

Solvatochromism

The term *solvatochromism* is used to describe the pronounced change in the position (and sometimes intensity) of a UV/Vis absorption that accompanies a change in the polarity of the medium. A hypsochromic (or blue) shift with increasing solvent polarity is usually called *negative solvatochromism*. The corresponding bathochromic (or red) shift is termed *positive solvatochromism*. A qualitative interpitation of solvent shifts is possible by considering (a) the momentary transition dipole moment present during the optical absorption, (b) the difference in permanent dipole moment between the ground and excited state of the solute, (c) the change in ground-state dipole moment of the solute induced by the solvent, and (d) the Franck-Condon principle

According to Bayliss and McRae, four limitation case be distinguished for intramolecular electonic transitions in solution[19] below:-

1. Nonpolar solute in nonpolar solvent: In this case, only dispersion forces contribute to the solvation of the solute. Dispersion forces, operative in any solution, invariably cause a small bathochromic shift, the magnitude of which is a function of the solvent refractive index, the transtion intensity, and the size of the solute molecules.

2. Nonpolar solute in polar solvent: In the absence of a solute dipole moment, there is no significant orientation of solvent molecules around solute molecule, and again a general red shift, depending on solvent refractive index is expected. Solute quadrupole/solvent dipole interactions have to be taken into account in this case.

3. Dipolar solute in a nonpolar solvent: In this case, the force contributing to solvation are dipole-induced dipole and dispersion forces. If the solute dipole moment increases during the electronic transition, the Franck-Condon excited state is more solvated by dipolar-solvent refractive index and the change in solute dipole moment, is expected. The Franck-Condon excited state is less solvated if the solute dipole moment decreases during the electronic transition, and a blue shift, again proportional to the two above-mentioned factors, is expected. In the latter case, the resultant shift may be red or blue depending on the relative magnitude of the red shift caused by polarization and the blue shift.

4. Dipolar solute in a polar solvent: Since the ground-state solvation results largely from dipole-dipole forces in this case, there is an oriented solvent cage around the dipolar solute molecules, resulting in a net stabilization of their ground state. If the solute dipole moment increases during electronic transition, the Franck-Condon excited state is formed in a solvent cage of already partly oriented solvent dipoles. The better stabilization of the exited state relative to the ground state with increasing solvent polarity will result in the bathochromic shift. Its magnitude will depend on the extent of the change in the solute dipole moment during the transition, the value of the solvent dipole moment, and the extent of interaction between the solute and solvent molecules.

If the dipole moment of the solute decreases during the electronic transition, the Franck-Condon excited state is formed in a strained solvent cage of oriented dipoles not correctly disposed for its efficient stabilization. Thus, with increasing solvent polarity, the energy of the ground state is lowered more than that of the excited state, and this produce a hyposochromic shift. The superimposed bathochrmic shift due to polarization will usually be less, resulting in net hypsochromic shift. Through experimental and theoretical investigations on a number of organic molecules, it has been observed that, the shape, position, and intensity of electronic absorption bands are affected by changes in solvent properties like polarity, dielectric constant, polarizability, acidity and the nature of solute solvent interactions[20].

McConnell (1952) had catalogued the solvents blue or red shifts of certain electronic absorption of solute molecules and assigned them as $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition, respectively. Blue shift transition originates from the fact that the solvent molecules are oriented around the solute molecules to fit with the ground state charge distribution of the solute molecules. On excitation, if the char-ge distribution changed markedly as in $n \rightarrow \pi^*$ transitions, the solvents molecule would not have position and orientation to bind with the excited state charge distribution. Blue shift will therefore be observed since in relation to non-polar solvents, a polar solvent will give greater solvation energy for the ground state of the solute than for the excited state[21].

1.3 Fluorescence Spectra

Fluorescence spectroscopy is a technique for evaluating the physical and chemical properties of a substance by analyzing the intensity and characteristics of light emitted in the form of fluorescence. Fluorescence occurs when a molecule absorbs photons from UV-visible light spectrum (200–900 nm), causing transition to a high-energy electronic state, and then emits photons as it returns to its ground state in less than 10^{-9} s. Some energy is lost within the molecule through heat or vibration so that emitted energy is less than the exciting energy; that is, the emission wavelength is always longer than the excitation wavelength. The difference between the excitation and emission wavelengths is called a *Stokes shift*[22].

Phenomena of Fluorescence

Fluorescence spectroscopy is a form of analysis that utilizes the emission properties of specific molecules rather than their tendency to absorb certain wavelengths of light. This very fact makes it inherently more selective than absorption spectroscopy, because all molecules that fluoresce must absorb, but not all molecules that absorb necessarily fluoresce. Therefore, only specific types of molecules studied using fluorescence spectroscopy. First, it must be recognized that absorbance and emission (fluorescence) spectroscopy are closely linked. In order to have fluorescence, a molecule must be in an excited state, and in most cases, this can achieved through the absorption of a photon that is equal to the energy gap between the ground state of the molecule and some excited state. Once the molecule is excited, a number of relaxation pathways are possible that allow the excited molecule to release its excess energy. In many cases, the relaxation is a thermal process in which heat evolves. However, it is also possible that the molecule will emit a photon in order to dissipate the excess energy and the process called fluorescence. A molecule in the electronically exited state can be a completely different chemical species with its own wave function and nuclear geometry. Since the charge distances are different, it shows a different chemistry from the normal ground state molecules, more so because it has excess energy but weaker bonds. Certain other physical properties like dipole moment, pK value, redox potential also differ in comparison to the ground state value. Excited states, in general, have less deep minima in their potential energy surfaces, indicative of weakening of attractive interactions. Usually the equilibrium internuclear distance increase and

some of the state may be completely repulsional, leading to direct dissociation on transition to them[6].

Transition state corresponds to a vibrationally exited ground state (*i:e:* ground state in a strained configuration), where as exited electronic states may contain no excess vibrational energy, but are still much higher in energy than the ground state. In fact a molecule in an exited state is best regarded as a completely new entity, only remotely related to the same molecule in the ground state. An exited state will have a completely different electron distribution from the ground state different geometry, and more than likely will undergo chemical reaction quite different from those of the ground state. Electronic states of organic molecules can be grouped into two broad categories, singlet states(S) and triplet states (T). A singlet state is one in which all of the electrons in the molecule have their spins paired. Triplet states are those in which one set of electron spin have become unpaired. Triplet states and singlet states differ significantly in there properties as well as in their energies. A triplet state will always lie lower in energy than its corresponding singlet state. Fluorescence usually occurs from the first singlet state (S_1) to the ground singlet state (S_o) electronic state by emission of photons. The $0 \rightarrow 0$ transition is generally the same for absorption and fluorescence. According to stokes' rule, the fluorescence maximum is always located at lower wave-numbers (higher wavelength) than the absorption maximum because of the loss in energy due to vibrational relaxation.

Due to the working of the Franck-Condon principle and thermal relaxation of vibrational modes, the fluorescence spectrum always observed on the red side of the absorption spectrum, in approximate mirror image relationship for polyatomic molecules. This red shift of the fluorescence implies that the emitted quanta are of lower energy than the absorbed quanta, i.e. $h_{vf} < h_{va}$, stokes′ shift. Under certain condition at high temperatures, when higher vibrational levels of the ground state are thermally populated, anti-Stokes effect ($h_{vf} > h_{va}$) may be observed. Generally, there is an overlap region between absorption and emission spectra[6].

Luminescence Processes

Luminescence processes interpreted only in terms of the exited state, from which luminescence emission occurs, and its relationship to the ground state of the molecule. Although the simple

picture of photon absorption by a molecule subsequent by a reemission of a photon to give luminescence seems to be quite straightforward, there are nonradiative processes, which precede and/or compete with photon emission.

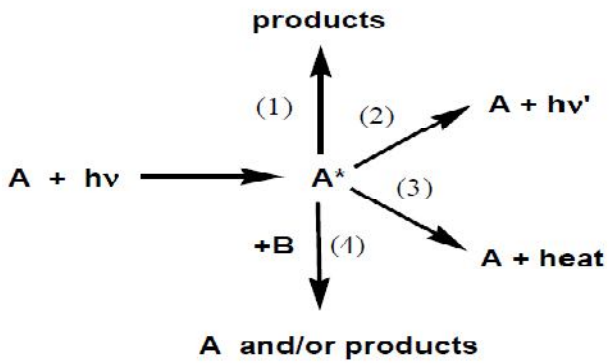
Generation of luminescence through excitation of a molecule by ultraviolet or visible light photons is a phenomenon termed photoluminescence, which is formally divided into two categories, fluorescence and phosphorescence, depending upon the electronic configuration of the excited state and the emission pathway. Fluorescence is a luminescence, in which absorption of a photon of radiation by molecular causes the emission of photon at a longer wavelength[16].

The absorption process is extremely rapid (10^{-15} sec), where as excited molecule to its ground state is taking 10^{-14} to several sec. Return to the ground state via molecular luminescence is among the slowest of processes in electronically excited states, requiring from 10^{-9} to a few sec. However, thermal equilibration by loss of vibrational energy is much faster requiring from 10^{-14}-10-^{12} sec. consequently, fluorescence and phosphorescence always originated from thermally equilibrated, electronically excited molecules being in the lowest vibratinal level (v = 0)[1].

The fundamental reaction in a photochemical or photophysical process is the absorption of a photon by a molecule. The excited state, which is formed is at a high energy level, unstable with respect to return to the lowest energy level (ground-state) by several possible deactivation processes.

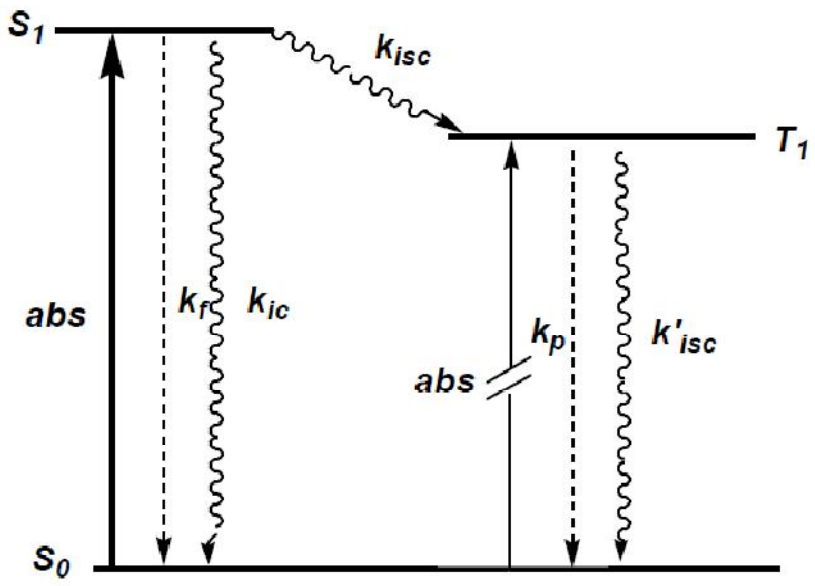
$$A + h\nu \rightarrow A^*$$

The excited state deactivation processes can be explained by a simple scheme (*Fig* 2) (1) dissociation of the original molecule and formation of products (photochemical reaction), (2) emission of light (radiative deactivation, also called luminescence), (3) dissipation of excess energy into heat (non-radiative deactivation), (4) interaction with other species in solution (quenching processes).



Figuer 2- Light excitation of a molecule and deactivation of the electronically excited state

Electronic spectroscopy shows that the probability of light absorption (corresponding to the intensity of the light absorption band) related to the quantum chemical characteristics of the states involved and particularly to their spin quantum number. Transitions from the ground states to excited states with the same multiplicity values are allowed and give rise to intense bands, whereas transitions to excited states of different multiplicity are forbidden and only have low intensity if observed at all in the absorption spectra. The majority of molecules are in the ground singlet state and the lowest excited state is often a triplet that cannot be directly populated by light absorption but can be obtained after relaxation of higher singlet excited states. We can summarize the relationship of the states involved in the photochemical process in a Perrin-Jablonski diagram (*Fig* 3); the deactivation by chemical reaction is not represented to simplify it. Emission of light (luminescence), is called fluorescence *f* or phosphorescence *p* and depends on the multiplicity of the excited and ground states. The radiationless deactivation is called internal conversion (ic) when it occurs between the same spin state and intersystem crossing when it occurs between states with different spin. Fluorescence and internal conversion are spin-allowed transitions, whereas phosphorescence and intersystem crossing are spin forbidden steps.



Figuer 3: - Perrin-Jablonski diagram, with energy levels for a simple molecular species. S_0, S_1,and T_1 are the singlet ground state, singlet excited state, and triplet excited state respectively; k_f, k_{ic}, k_{isc}, k_p and k'_{isc} are the rate constants for fluorescence, internal conversion $S_1 \Rightarrow T_1$ intersystem crossing, phosphorescence, and $T_1 \Rightarrow S_0$ intersystem crossing, respectively.

Isoemissive point

Isoemissive point defined as the wavelength or frequency at which all the emission spectra observed with a change in the parameter (time, temperature, pH, concentration etc.) has the same intensity. Isoemissive point in fluorescence spectroscopy is analogous to the isosbestic point in the absorption spectroscopy except that isosbestic point refers to two absorptive species in the ground state whereas isoemissive point refers to two emissive species in the excited state.

1.3.1. Factors affecting Fluorescence Spectra

Solvent

The important characteristics of the solvent are;

- Good solubilsing power
- Stable interactions with the absorbing species

From the optical point of view, the solvent should be transparent in the region, and should be of consistent purity.

Solvent effect in Fluorescence spectra

When excited states of molecules are created in solution by continues or flash excitation, the excited-state molecule interacts to a varying degree with the surrounding solvent molecules, depending on their polarity, before returning to the ground state. These excited-state solute/solvent interactions found in fluorescent molecules often reflected in the spectra position and shpe of the emission bands as well as in the lifetimes of the excited-state molecule. The solvent-dependence of the position of emission bands in the fluorescence spectra is commonly included in the term solvatochromism. Sometimes, the solvent-dependence of fluorescence spectra has been called fluorosolvatochromism[20].

When the dipole moment of a fluorescent molecule is larger in the excited state than in the ground state(i.e. $\mu_e > \mu_g$), then the differential salvation of the two state by solvent of varying polarity gives rise to an increase in the Stokes' shift with increasing solvent polarity[16,23]. When considering the solvent dependence of the position of emission bands, the finite relaxation time τ_R for the rearrangement of the solvent molecules surrounding the solute molecule in the Franck-Condon excited state and the finite lifetime τ_e of the molecule in the excited state have to be taken into account. In fluorescent molecules, subsequent to excitation to the Franck-Condon excited state, the ground state solvent cage reorients itself to conform to the new electronic distribution of the excited molecule. This solvent relaxation process involves reorientation of solute dipoles about centers of positive and negative charge in the excited molecule, and possibly the strengthening, weakening, breaking and making of hydrogen bonds. Because nuclear motion are involving, solvent relaxation is approximately contemporaneous with vibration relaxation, taking about 10^{-14}-10^{-12} sec, and is rapid by comparison with the lifetime of the lowest excited singlet state (approximately, 10^{-8}).

Numerous theoretical and experimental studies of solvent effect on the fluorescence spectra of organic molecules (fluorophores) have led to a variety of quantitative expression. Among the existing relationships describing how a change in dipole moment ($\Delta\mu = \mu_e - \mu_g$) correlate with

electronic excitation and emission, the most popular are based on a linear correlation between the difference in wave numbers of the absorption, fluorescence maxima ($\Delta\nu = \nu_a - \nu_f$ = stokes shift), and a solvent polarity function which usually involves the relative permittivity ($\in_r$), and the refractive index (n) of the medium. Liptay has developed the equation below for solvent dependence of the difference between the wave numbers of the absorption (g→e) and the corresponding emission (e→g). All terms depending on polrizabilty change are neglected.

$$\nu_f = \nu_a - \frac{2\mu_g(\mu_e - \mu_g)}{4\pi\ \varepsilon_o hca^3}\left[\frac{\in_r - 1}{2\ \in_r + 1} - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right]$$

where h is the Planck's constant, c is the speed of light, and a is the radius of the cavity in which the fluorophore resides and , μ_e and μ_g are excited and ground state dipole moments, respectively. The red shift observed in the fluorescence spectra with an increase in solvent polarity depends on the difference in permanent dipole moments of the ground and excited state, and this is in accordance with the theory of dielectric polarization. The effect of solvent polarity on the fluorescence shift was utilized to infer the charge separation of fluorescence molecule in the excited state[18,23].

Acidity Effect on Electronic Spectra

Addition of acids or base to the solvent in which absorbing, fluorescing or phosphorescing molecules (having functional groups with dissociable protons or lone pair or nonbonding electron pairs) are studied, can affect the electronic spectra in two ways. If the acidity of the medium after addition of acid or base is insufficient to proton from a dissociable group, the acid or base may form hydrogen boding with the basic or acidic groups of the molecule of spectroscopic interest. The effects of these types of hydrogen bonding upon the electronic spectra are similar to those described for hydrogen bond donor and acceptor solvents. Thus the additions of small amounts of trifluoroacetic acid to solutions of aromatic carboxylic acids in hydrocarbon solvent or of small amounts of 1,4-dioxane to the solutions of phenols in hydrocarbon solvents produce shifts to longer wavelengths of the absorption and fluorescence spectra. Several nitrogen heterocyclic such as quinoline and acridine and some aromatic carbonyl compounds such as 2-acetonaphthone and pyrene-3-aldehyde do not fluoresce but phosphoresce in hydrocarbon

solvent. The addition of small amounts of acids such as trifloroacetic acid or trichloroacetic acid which are fairly soluble in hydrocarbons, result in the appearance of fluorescence and a decrease in the intensity of phosphorescence from these molecules[1].

pH Effects

Relatively small changes in pH will sometimes radically affect the intensity and spectral characteristics of fluorescence. Most phenols are fluorescent in neutral or acidic media, but the presence of a base leads to the formation of nonfluorescent phenate ions. 5-hydoxyindoles for, example, show a shift in fluorescence emission maximum from 330 nm at neutral pH to 550 nm in strong acid without any change in the absorption spectrum [24].

Coordination by metal Ions

The coordination of fluorescing or phosphorescing aromatic ligands by metal ions is actually an acid-base reaction, with the metal ion acting as a Lewis acid (electron pair acceptor) and the ligand acting as a Lewis base (electron pair donor). In this regard, the coordination of ligands by metal ions is analogous to the protonation of the ligand, in which case, the hydrogen ion function as the Lewis acid. As a result, it might be expected that many of the change of the electronic spectra of the ligands, produced by metal ion coordination, will be analogous to the pH and Hammett acidity dependence of ligand spectra described. The coordination of aromatic ligands by non-transition metal ions (e.g. Zn(II), Cd(II) Al(III), Ga(III)) has the effect of producing positive polarization at the coordination sites on the ligand and the spectral shifts that are produced by coordination with these ions are similar to the shifts produced by protonating the ligand at the coordination site[1].

Solvent Effects on Conformational Equilibria

Changing the medium has a particular effect on various conformational and rotational equilibria. Because the Gibbs energy differences between conformational isomers are almost very small (ca. 0 to13 kJ/mol) and the solvation enthalpies of dipolar solutes are at least as large and often much larger than this, the medium can affect conformational equilibria very considerably. It is often found that one conformer or rotamer is predominant in one medium but not in another. This has

led to the long established rule that the conformer (rotamer) of higher dipole moment is more favored in media of high dielectric constant[20].

Quenching of Molecular Luminescence

Fluorescence or phophorescence intensites may be quenched (diminished or even eliminated) due to the deactivation of the excited state responsible for luminescence by interaction of either the ground or excited states of the luminescing species with other species in solution. The mechanisms of luminescence quenching are not completely understood but reversible electron transfer appears to be involved in quenching by species with low ionization potentials or electron affinities (e.g. molecular oxygen, transition metal ions and other paramagnetic or highly conjugated species)[25]. On the other hand, evidence is being accumulated that quenching by interaction with the solvent, or by interaction with hydrogen bonding molecules proceeds by a vibrational mechanism; the interaction between the luminescing molecule and the solvent providing vibrational coupling which favors efficient internal conversion[1].

Concentration Effect

For the spectra behavior of molecule in solution were based upon the behavior of molecules in very dilute solutions (10^{-4} M) where the interaction were predominantly of solute-solvent type. High concentrations of absorbing or luminescing species, in solution, may cause problem in the interpretation of molecular electronic spectra. Some of these problems arise from instrumental consideration and must be dealt with from a practical point of view. However, some aspects of the spectroscopy of concentrated solutions arise from solute-solute interactions and their consideration is fundamental to the understanding of chemical spectroscopy.

Temperature Effects

Changes in temperature affect the viscosity of the medium and hence the number of collisions of the molecules of the fluorophore with solvent molecules and the strength of hydrogen bonding. Fluorescence intensity is sensitive to such changes and the fluorescence of certain fluorophores shows temperature dependence. In such cases, the use of thermostatted cell holders are recommended. Normally, it is sufficient to work at room temperature with the provision that any

sample procedure involving heating or cooling must also allow sufficient time for the final solution to reach ambient before measurement .

Adsorption, Photodecomposition and Oxidation

Loss of organic substances by adsorption onto the walls of the container becomes particularly troublesome at the sub-microgram level. New glass surfaces should be thoroughly cleaned in acid before use and measurements of aromatic substances in nonpolar solvents should be avoided. Often the addition of a small quantity of a polar solvent to a non-polar one will greatly reduce adsorption losses. Fluorimeters employ intense light sources to produce high sensitivity and in some cases, the level of incident light may be sufficient to decompose the sample under investigation.

1.4 Computational Method

Computational chemistry simulates chemical structures and reactions numerically, based in full or in parts on the fundamental laws of physics. It allow the chemists to study chemical phenomena by running calculation on computers rather than by examining reactions and compounds experimentally some methods can be used to model not only stable molecules, but also short lived, unstable intermediate even transition state. There are two broad areas within computational chemistry devoted to structures of molecules and there reactivity: molecular mechanics and electronic structure theory, they both perform the same basic type of calculation[26].

There are two approaches to modeling spectroscopic features, ab initio and semi-empirical methods. Traditionally, chemists have found that ab initio techniques are entirely too expensive in terms of time because they use the Schrödinger equation without any further experimentally obtained approximations. Semi-empirical methods use parameters from experimental data, simplifying the approximation of the Schrödinger equation and lowering the expense of the calculation. In two of the Fabian papers[27,28], abinitio calculations were compared to various semi-empirical methods and the less expensive semi-empirical methods were actually found to be more accurate than the abinitio in the prediction of both absorption and emission spectra.

Therefore, in the past, semi-empirical methods have been used because they have shown to be both inexpensive and sufficiently accurate for many applications.

Semi-empirical methods that have been applied to relatively large chemical systems for over three decades. Abinitio methods unlike either molecular mechanics or semi empirical methods use no experimental methods in their computations instead their computations are based slowly on the law of quantum mechanics.

Optimization

Computing the energy of particular molecular structure (spatial arrangement of nuclei and electrons). Properties related to the energy may also be predicted by some method performing geometry optimizations, which locate the lowest energy molecular structure in close proximity to the specified starting structure geometry, optimizations depend primary on the gradient of energy -the first derivate of the energy with respect to atomic positions. This usually results in finding a local minimum of the energy. This local minimum corresponds to the conformer that is closest to the starting geometry.

Potential energy surface

A potential energy surface (PES) is a geometric hypersurface on which the potential energy of a set of reactants is plotted as a function of the coordinates representing the molecular geometries of the system. The PES is the most complete description of all the conformers, isomers, and energetically accessible motions of a system. Minima on this surface correspond to optimized geometries. The lowest-energy minimum is called the global minimum. There can be many local minima, such as higher-energy conformers or isomers[26].

2. Objective, Materials and methods

2.1 Objectives

General objective:

To investigate photophysical properties of the cis-trans 2,2′- biquinoline molecules those existing in equilibrium

Specific objectives:

The specific objectives of this study include investigation and

- Determination of fluorescence emission spectra of 2, 2′- biquinoline.
- Comparison of absorption spectra and fluorescence emission spectra.
- Determination of effect of solvents on the absorption and fluorescent emission spectra.
- Identification of structural features responsible for the dual fluorescence.
- Computation of important physical properties of 2, 2′- biquinoline.

2.2. Materials and Method

2,2′- biquinoline (Sigma-Aldrich) was used without further purification; and cyclohaxane (Riedel-de Haen), 1,4-dioxane (Aldrich), acetonitrile (Sigma-Aldrich), dichloromethane (Timstar-Laboratory Suppliers), butanol (BDH) were used as solvent. Acetone was used for cleaning purpose. For complexation anhydride zincnitrate and for pH adjustment hydrochloric acid HCl (Riedel-de Haen) were used. 2, 2′- biquinoline was taken from store and absorption spectra of the solutions were recorded on a SPECTRONIC GENESYS 2PC UV-Vis spectrophotometer containing deuterium and tungsten lamp as light source for different spectral regions and the results have good absorption in the UV-V's region. Before measuring the absorption spectrum of the sample, the base line corrections were done by placing solvent in quartz cuvette of 1 cm. The fluorescence emission and excitation spectra were recorded with Fluoromax-4 (Jobin Yvon) spectrofluorometer that have xenon lamp as light source. Both UV-Vis and spectrofluorometer are connected to a personal computer. Quartz cuvettes in the right

angle arrangement were used as sample holder in making the measurements. Emission spectrum was recorded by fixing the excitation wavelength and scanning the emission wavelength over the range of interest. Similarly, excitation spectrum was recorded by fixing the emission wavelength and scanning the excitation wavelength. To investigate the effect of pH, dilute HCl was added to solution of 2, 2′- biquinoline in acetonitrile . De-ionized water was used for the preparation of the HCl solutions. Post data processing was done by using Origin.6 software. In the data analysis, the Raman and Rayleigh peaks were deleted from the excitation and emission spectra.

Computational Method

Quantum Chemical calculations were performed at Semi-empirical of INDO methods levels of theory with the Gaussian 03 package.13. Geometries were optimized at DFT levels with the STO-3G basis set with no symmetry constraints.

3. RESULTS AND DISCUSSION

3.1. Experimental

3.1.1. Absorption Spectra of 2, 2′- biquinoline

Absorption spectra of 2, 2′- biquinoline samples has been recorded in solvents of different polarity, the results are also analyzed by drawing the normalized spectrum (for each spectrum, the intensity values of the spectrum had been normalized with respect to the highest intensity peak of the corresponding spectrum). Since electronically excited states interact readily with neighboring molecules fine structure resulting from vibrational and rotational transitions are typically observed. 2,2′-biquinoline solution absorption spectrum shown in figure (4) in cyclohexane and n-hexane distinct band positions in 230-350 nm region having 0-0 band at around 324 nm and a prominent high energy band at 257 nm is from the transition of $S_o \rightarrow S_2$ which is strong and have large intensity, and along with the vibrational band at around 313 nm and 336 nm.

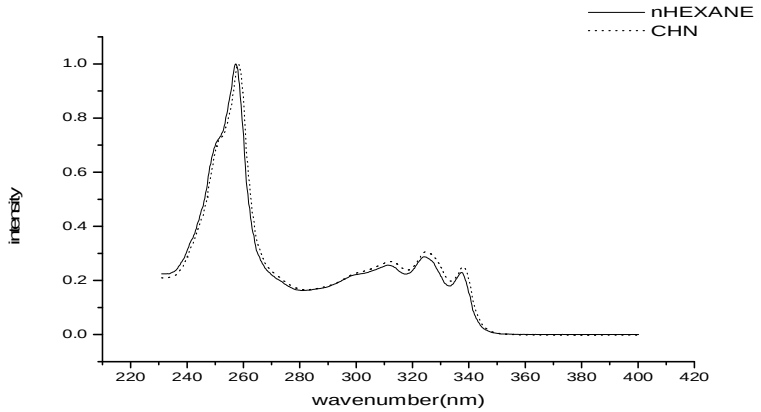


Figure 4:- Peak normalized absorption spectra of 2, 2′- biquinoline in cyclohexane and n-hexane

The normalized spectra of 2, 2′- biquinoline in different solvents are represents in Figure (5) and the values are tabulated in Table 1 for each band observed in the spectra. It has been established experimentally that only those molecules with π-electrons for which the charge distribution (and consequently the dipole moment) in the electronic ground state is considerably different from that in the exited state exhibit a pronounced solvatochromism[20]. This way the spectra of 2, 2′- biquinoline show only a slight shift in the wavelength of maximum absorption (λ_{max}) bands relative to that observed for cyclohexane and n-hexane . The recorded band shifted in different solvent was within the range of 324 - 327 nm. A hump like band for dichloromethane at 365 nm was observed.

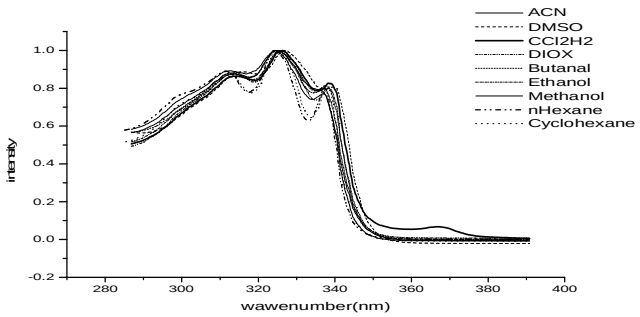


Figure 5:- Peak normalized solvent effect on the absorption spectra of 2, 2′- biquinoline in different solvent

Table 1: Values of absorption maxima of 2, 2′- biquinoline in solvents of different polarity

Solvent	λ_{max} (nm)
Acetonitrile	324.6
Dimethylsulfoxide	327.4
Dichloromethane	326.1
Dioxane	325.2
Butanal	325.5
Ethanol	324.6
Methanol	324.9
n-Hexane	324.3
Cyclohexane	324.4

In Table 1, the small change 324.4-327.4 nm, indicates that the solvent-solute interaction that alters the energy difference between the ground and excite states are relatively small when the polarity of solvents changes.

3.1.2. Effect of metal ion on the absorption spectra of 2, 2′- biquinoline

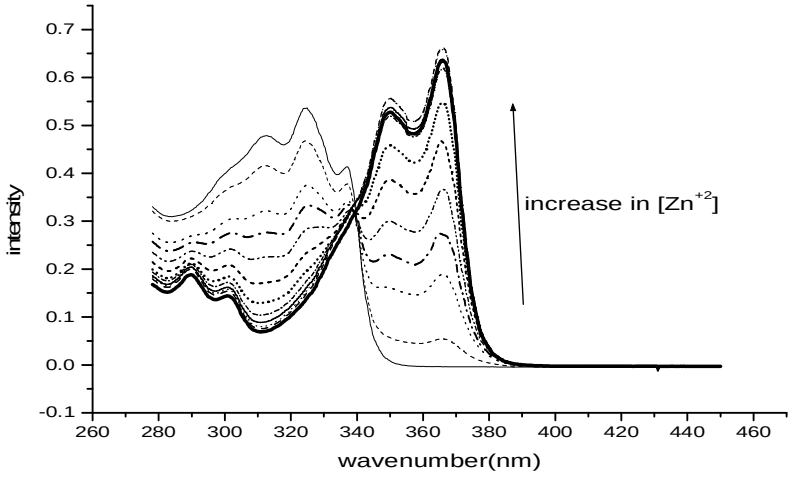


Figure 6:- Area normalized absorption spectra of 2, 2′- biquinoline in acetonitrile at different Zn^{2+} ion concentrations added drop wise, $[Zn^{+2}] = 2.3x\ 10^{-5}$

The coordination of fluorescing aromatic ligands by metal ions is actually an acid-base reaction, with the metal ion acting as a Lewis acid (electron pair acceptor) and the ligand acting as a Lewis base (electron pair donor). As a result, it might be expected that many of the change of the electronic spectra of the ligands, produced by metal ion coordination[1]. Titration of 2,2'-biquinoline solution in acetonitrile with a less concentrated zinc solution showed a gradual increase in the absorbance of the metal chelate compound and a decrease in the absorbance of the metal free ligand indicating that the more stable trans conformer is being converted to cis metal chelated form.

Absorption spectra of metal chelated ligand (figure 6) showed peak maxima that have 0-0 band at 366 nm, along with the vibrational band at 350 nm and 325 nm, along with the vibrational band at 313 nm, 337 nm with an isosbestic point at 338 nm. Increasing Zn^{2+} ion concentration increases the intensity of the band at 366 nm whereas the band at 325 nm decreases. The intensity changes with Zn^{2+} ion concentration observed for both bands indicates the change of the metal-free 2,2'-biquinoline (band at 325 nm) to the metal-chelated complex (band at 366 nm). The presence of isosbestic point verifies existence of two absorbing species in equilibrium at the ground electronic state. Since the presence or absence of metal ions in solutions of 2,2'-biquinoline switches between the cis/trans conformations; the band at 366 metal-chelated 2,2'-biquinoline of cis form, the band at 325 nm can be assigned to be originated from the metal free trans structure of 2,2'-biquinoline. Generally, aromatic molecules complexed with closed shell diamagnetic metal ions such as zinc, cadmium and gallium fluorescence strongly, with fluorescence spectra similar to the chromospheres. The lowest excited states of metal complexes of Zn^{2+} with ligand are well known to possess ligand-localized states[1].

3.1.3. **Effect of pH on the absoption spectra of 2, 2′- biquinoline**

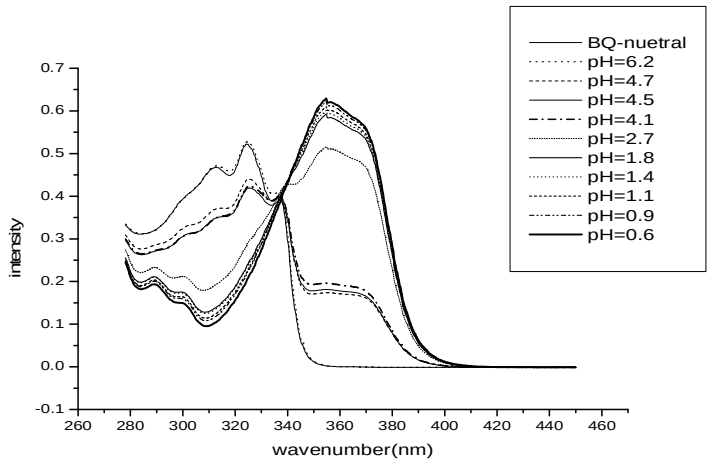


Figure 7:-Area normalized absorption spectra of 2, 2′- biquinoline at different pH in acetonitrile.

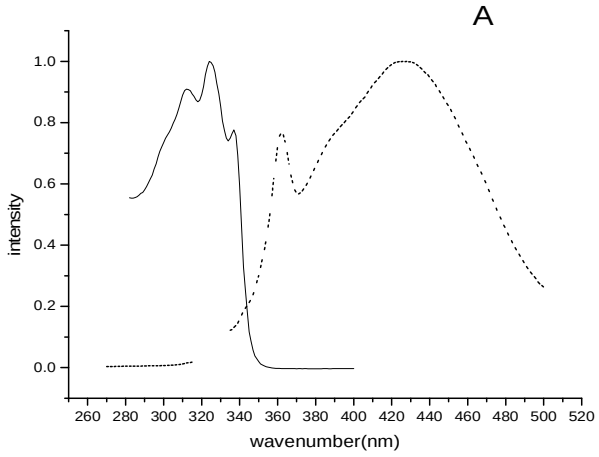
The coordination of ligands by metal ions is analogous to the protonation of the ligand, in which case, the hydrogen ion function as the Lewis acid[1]. As a result of the acido-basic properties in the ground and excited states, absorption and fluorescence spectra are pH-dependent [16]. The effect of pH on the absorbance of 2,2'-biquinoline was presented in Figure 7 showing a shift in the absorbance bands from 325 nm (along with vibrational band) to 356-368 nm for the longer wavelength. Stepwise decreases in pH of the 2,2'-biquinoline solution in acetonitrile increases the intensity of the longer wavelength band and decreases the intensity of the 325 nm band with an isosbestic point at 338 nm.

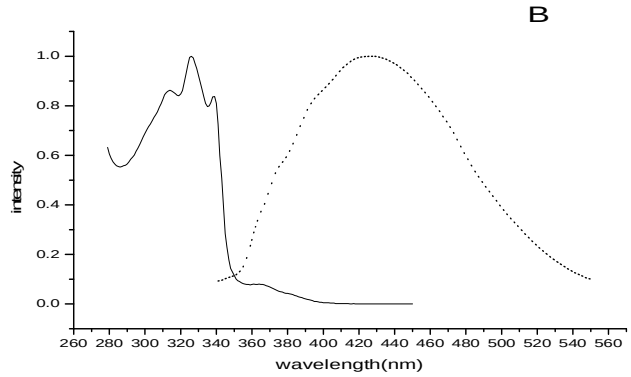
In absorption spectra, the similarity between the acidified 2,2'-biquinoline solution and the metal-chelated spectra indicates that the monocation forms predominantly exists in solution has a cis structure. The presence of the isosbestic point and change in intensity of the bands with pH also shows the interconversion of cis/trans structures present in equilibrium at around isosbestic point. In line with the metal, the monoprotonated 2,2'-biquinoline is of cis structure that has relatively similar absorption wavelength maxima to the metal-chelated complex. Therefore, the mono-protonated 2,2'-biquinoline that forms in acidic solution has a cis structure with the absorption spectra maxima around 356-368 nm which is broad.

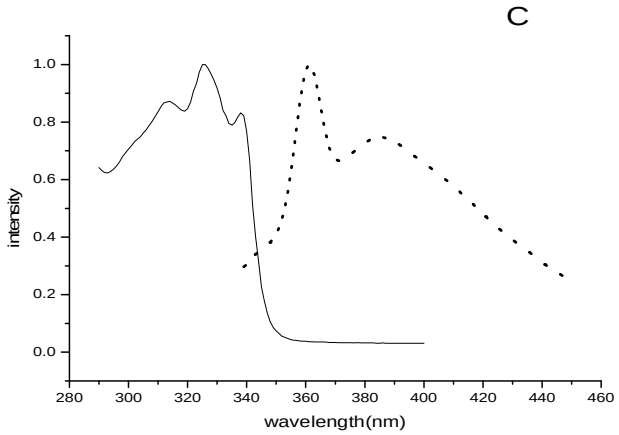
3.1.4. Fluorescence and Absorption spectra of 2,2'-biquinoline

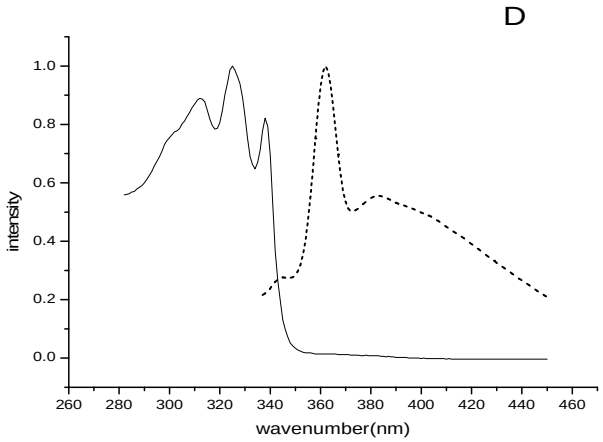
Due to the working of the Franck-Condon principle and thermal relaxation of vibrational modes, the fluorescence spectrum is always observed on the red side of the absorption spectrum, in approximate mirror image relationship for polyatomic molecules[6]. Fluorescence (emission at excitation of their λ_{max} of absorption) and absorption spectra of 2,2'-biquinoline in different solvent show similarity in their band shape. As shown in Figure 8, in all solvents their band shape is similar but there is a difference in the position of the long wavelength bands between the fluorescence and absorption spectra and broding in fluorescence spectra shows that influence of the intermolecular and intarmolecular interaction forces may not be resolved in absorbance spectrum as in fluorescence spectrum case for brodinig (Figure 8).

When the dipole moment of a fluorescent is larger in excited state than in the ground state (i.e. $\mu_e > \mu_g$) the differential solvation of the two state by solvent polarity gives rise to an increase in the Stokes' shift with increasing solvent polarity[20]. Stokes' shift values are tabulated in Table 2









Figuer 8:- fluorescence (- - -) and absorption (__) spectra of 2,2'-biquinoline in acetonitril (A), Dichloromethane (B), 1,4- dioxane (C) and Cyclohexane D.

Table 2: Values of absorption emission and Stokes shifts at λ_{max} of 2, 2′- biquinoline in solvents of different polarity

Solvent	Absorption λ_{max}	Emission λ_{max}	Stock shift
Cyclohexane	324.2	359	34.6
P-dioxane	325.2	366	40.8
Acetonitrile	325.6	425	100.4
Dichloromethane	326.1	426	99.9

3.1.5. Excitation Spectra of 2,2-biquinoline

The variations in fluorescence intensity as a function of the excitation wavelength for a fixed observation wavelength represents the excitation spectrum. For a single transition the band shape of absorption and excitation spectra are similar, provided that there is a single species in the ground state. In contrast, when several species are present, or when a sole species exists in different forms in the ground state (aggregates, complexes, rotamers, tautomeric forms, etc.), the excitation and absorption spectra are no longer superimposable [16]. Thus, any pronounced variation, in the band shape, indicates the existence of more than one transition, which may be attributed to the existence of multiple absorbing species. Since in the excitation spectrum, only the bands corresponding to the fluorescent species are observed, difference between the absorption and excitation spectra may result. Furthermore, in the absorption spectrum, the bands corresponding to the various species may not be resolved when the electronic structure of the excited species are closer; and also influence of the intermolecular and intramolecular interaction forces may not be resolved in absorbance spectrum as in excitation spectrum. Consequently, broadened band is observed. As cited in the theoretical section, 2,2'-biquinoline is a compound that exists in cis/trans isomeric forms, thus difference between the two (absorption and excitation) is expected.

3.1.6. Effect of metal ion on Excitation spectra 2,2'-biquinoline

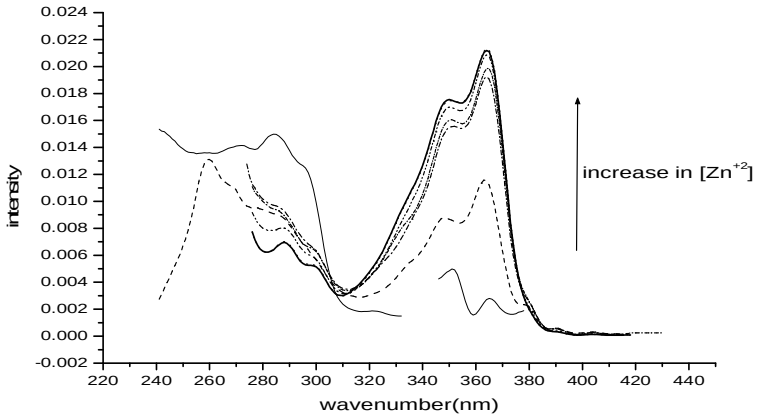


Figure 9:- Effect of metal ions on the excitation spectra of 2,2'-biquinoline in acetonitrile, λ_{Em} = 430 nm. (Area normalized uncorrected excitation spectra).

Excitation spectra of metal chelated ligand showed peak maxima at 364 nm and 290 nm with an isosbestic point at 307 nm. Increasing Zn^{2+} ion concentration increases the intensity of the band at 364 nm whereas the band at 290 nm decreases. Compared to the absorbance spectra (Figure 6), relatively similar band shape and absorption maxima were observed. The intensity changes with Zn^{2+} ion concentration, which is added drop wise observed that indicates the change of the metal-free 2,2'-biquinoline (band at 290 nm) to the metal-chelated complex (band at 364 nm). The presence of isosbestic point verifies existence of two absorbing species in equilibrium at the ground electronic state. Since the presence or absence of metal ions in solutions of 2,2'-biquinoline switches between the cis/trans conformations; and metal-chelated 2,2'-biquinoline is of cis form, the band at 290 nm can be assigned to be originated from the metal free trans structure of 2,2'-biquinoline.

3.1.7. Excitation spectra in different Solvents

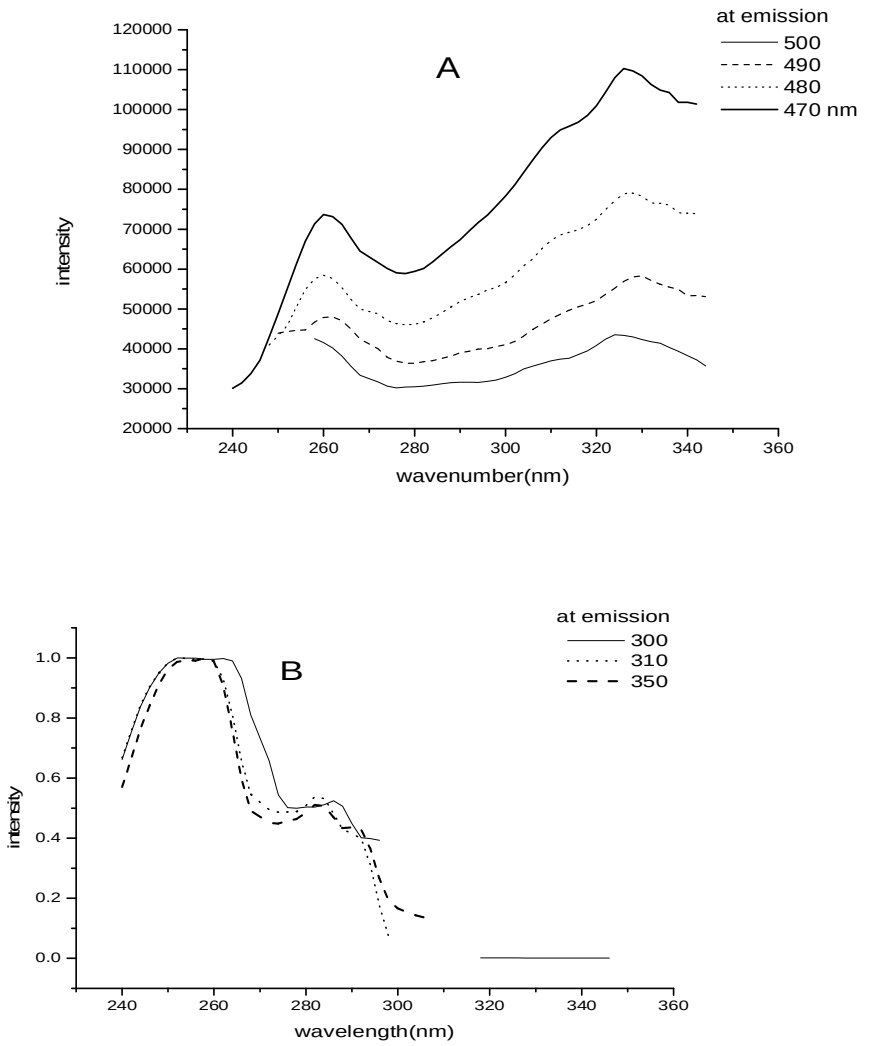


Figure 10 :- Uncorrected excitation spectra of 2,2'-biquinoline in cyclohexane, at higher emission (A) and lower emission (B)

The relative intensity of the short wavelength ($S_0 \rightarrow S_2$) excitation band predominates in the non-polar solvent, cyclohexane in lower emission but in higher emission the $S_0 \rightarrow S_1$ excitation band is predominant and it have higher intensity than the lower emission (figure 10)

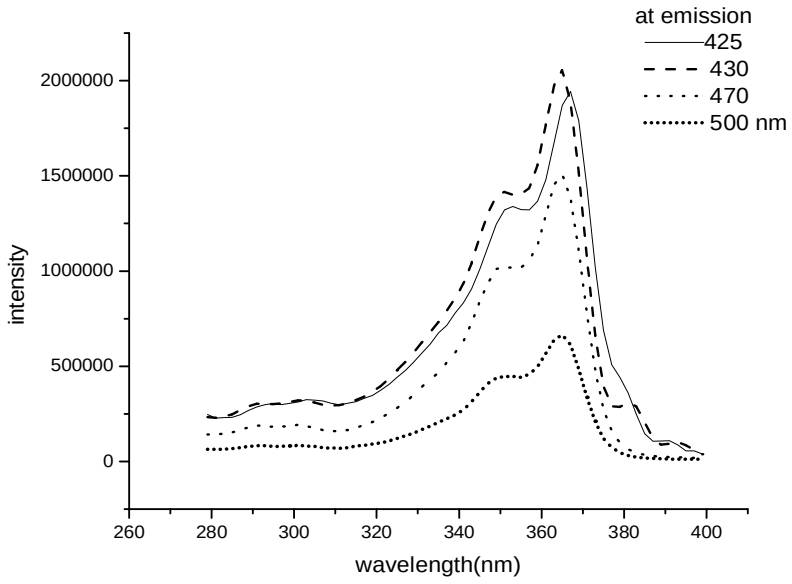


Figure 11:- Uncorrected excitation spectra of 2,2'-biquinoline in acitonitrile, at higher emission

At higher emission, the excitation and absorption bands during addition of metal ion are almost similar in their λ_{max} and band shapes i.e. almost the shift is insignificant. In Figure 11 presents the excitation spectra of 2,2'-biquinoline for varying emission wavelengths from 425-500 nm. Upon increasing the emission wavelength from 425 nm to 500 nm, the excitation spectra showed two bands depending on the emission wavelength. On increasing the emission wavelength, the intensity of the lower energy band progressively increases while the intensity of the higher energy band decrease, with respect to each other. The intensity of the higher energy band much smaller than the intensity of lower energy band which have the same result like when addition of the highest drop wise Zn^{+2} ion (Figure 6).

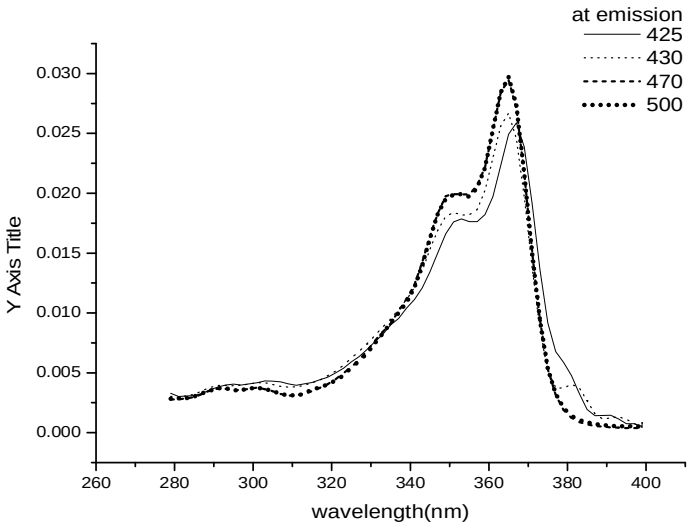


Figure 12: Peak normalized uncorrected excitation spectra of 2,2'-biquinoline in acitonitrile solution

In Figure 12 distinct isosbestic point (a common point between two components of absorption, i.e., a point of equilibrium) observed at 336 nm, is a clear indication of an equilibrium condition of population density between the ground absorption states.

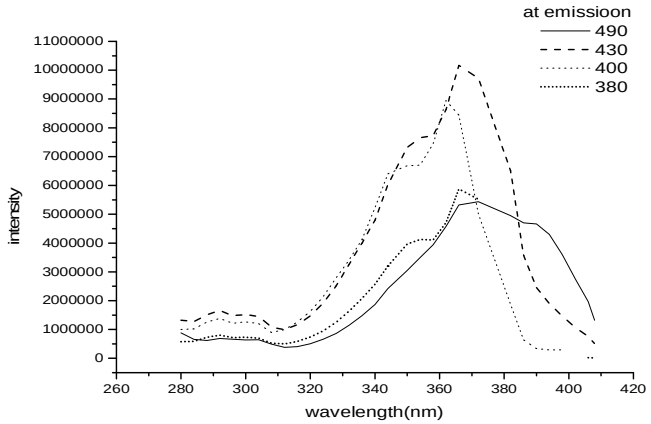


Figure 13:- Uncorrected excitation spectra of 2,2'-biquinoline in Dichloromitane,, at higher emission

In Figure 13 presents the excitation spectra of 2,2'-biquinoline for varying emission wavelengths from 380-490 nm. Upon increasing the emission wavelength from 380 nm to 390 nm, the excitation spectra showed two bands depending on the emission wavelength. At higher emission, the excitation and absorption bands during addition of metal ion are almost similar in their λ_{max} and band shapes i.e. almost the shift is insignificant, this shows that at higher emission the cis conformer is more stable than the trans one but the band for tans is much less intense from the cis one, also see Figure 6 and 9

In similar way, the same reason for acetonitrial is true for dichloromethane, this shows that the nature of solvent determines the nature of the species that emits within the ranges stated. Therefore one can conclude that, in cyclohexane, one absorbing species predominates in the ground state, but in acetonitril and dichloromethane two absorbing species are predominat in the ground state.

3.1.8 **Emission Spectra of 2,2'-biquinoline**

The fluorescence spectra of this compound are not as simple as its absorption spectra. The influence of polarity on fluorescence emission spectra were dealt with although explanation of what is observed is more complex. A series of emission spectra of 2,2'-biquinoline were obtained at different excitation wavelengths in solvents cyclohexane, acetonitrile, Dichloromethan and p-dioxane . Generally, if the solute molecule becomes more polar in the excited state, there will be greater electrostatic stabilization of the excited states, relative to the ground state by interaction with the polar solvent. The greater the polarity of the solvent, the lower will be the energy of the Frank-Condon (FC) excited state. Solvent effects on the absorption spectra of 2,2'-biquinoline was found to be small. However, fluorescence spectrums were found to depend greatly on the polarity of the solvents used. Since fluorescence usually takes place from equilibrated excited states, excited electrons from higher energy levels usually relax to the lowest excited states, S_1, via internal conversion or vibrational relaxation. Compared to the time required for electrons to transit from ground state to one of the higher energy excited electronic states, solvent relaxation takes longer time. After excitation has taken place, solvents reorient themselves around the excited molecule leading to decrease in the energy of the excited state.

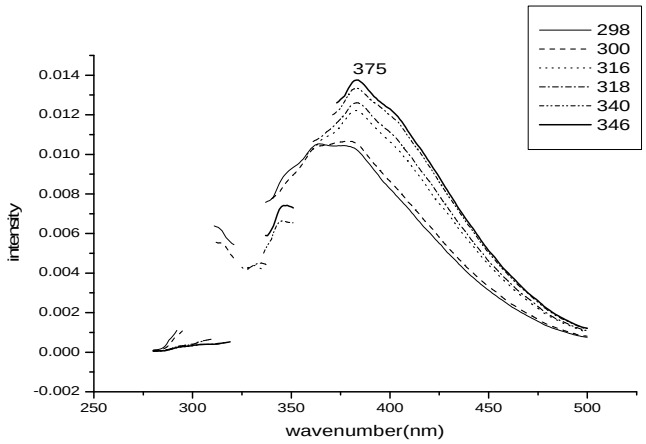


Figure 14:- Peak normalized emission spectra of 2,2'-biquinoline in Cyclohexane

The emission spectra of 2,2'-biquinoline in cyclohexane showed only one emission band at 375 nm (Figure 14). This shows that the nature of solvent determines the nature of the species that emits within the ranges stated. Therefore, one can conclude that, in cyclohexane, one absorbing species predominates in the ground state, or only one species responsible in the ground state that is stabilize in non-polar cyclohexane solvent.

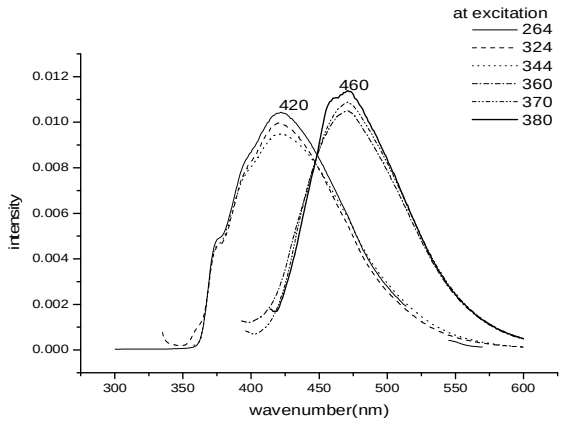


Figure 15:- Peak normalized emission spectra of 2,2'-biquinoline in Dichloromethane

Figure 15 represents the emission band of 2,2’-biquinoline in a solution of a polar solvent, dichloromethane, up on excitation at different wavelengths. The spectra show dependence on the excitation energy up on changing the excitation wavelength from 250 - 420 nm. From the figure, it can be observed that intensity and position of the two bands seem to depend significantly on the excitation energy in the ranges used. As the excitation wavelength increases the intensity of the longer wavelength band increases at the expense of the shorter wavelength emission band. For excitation wavelengths above 360 nm, only the longer wavelength band was observed. This change is an indicative of the absence of the mother-daughter relationship between the two emission bands and thus the observed excitation wavelength dependence of the emission spectrum can be attributed to different species in the electronic ground state present in the solution. Furthermore, their relative intensities dependence on the excitation wavelength violates the Kasha Rule stating that the same emission spectrum was generally observed irrespective of the excitation wavelength; i.e. a single excitation band gives rise to a single emission spectrum. And normalized emission spectra in the wavelength range 264 nm-400 nm gives an isoemissive point centered at 448 nm (Figure 15), indicating two emitting states originating from two equilibrium structures of a molecule in the ground state.

The 3D emission spectra of 2,2'-biquinoline in dichloromethane exhibited two maxima centers in the contours map (Fig. 16). The first maximum center appeared at excitation wavelength of 264 nm and the corresponding emission wavelength of 420 nm, whereas, the second maximum was centered at 370 and 460 nm excitation and emission wavelengths, respectively. This observation further confirms the presence of two ground state species in equilibrium in dichloromethane.

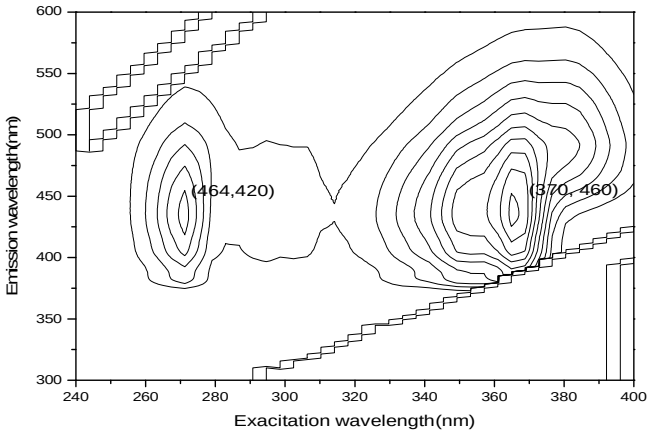


Figure 16:- Contour plot of 2,2’-biquinoline in dichloromethane solution.

Since excitation spectrum depends on emission wavelength and vice versa, it is possible to identify which excitation band corresponds to the low or higher energy emission band. In dichloromethane, the 3D spectra of 2,2'-biquinoline gives two contour centers (Figure 15). From metal complex (figure 6) and the excitation spectra (figure 12) that shows two different species in higher and lower emission; the excitation band observed at lower emission corresponds to the trans conformer, and excitation at higher emission corresponds the cis conformer. The emission and excitation spectra of 2,2'-biquinoline in dichloromethane together with the 3D emission spectra validate the existence of two absorptive species exciting at different wavelengths resulting in two emissions.

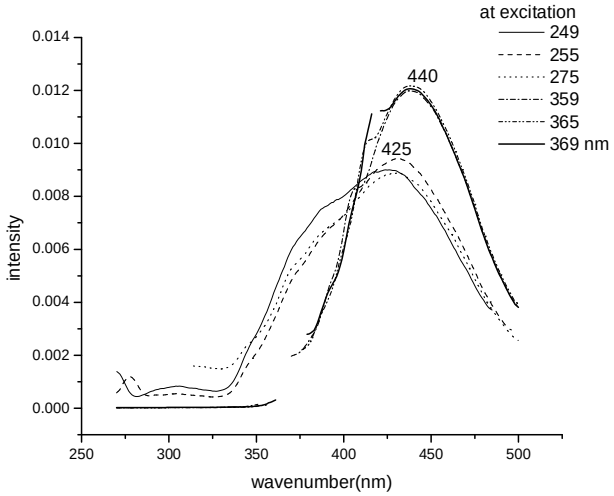


Figure 17:- Peak normalized emission spectra of 2,2'-biquinoline in Acetonitriale

In Figure 17 the emission spectra of 2,2'-biquinoline in Acetonitrile at the excitation wavelength range of 249 to 369 nm are presented. In this excitation spectra range, both emission bands and strong excitation wavelength dependence, i.e. change in cis and trans conformer ratio, were observed. It suggests that the presence of more than one structures in the ground state that are responsible for the observed dual fluorescence. During proportion of change of the cis and trans conformer emission bands in the excitation wavelength range of 249 to 369 nm the excitation wavelength increases from 249 to 275 nm, the intensity of the trans conformer is dominant (see also, figure 6,7,10 and 11),. From 359 nm onwards or in higher emission the intensity of cis conformer.

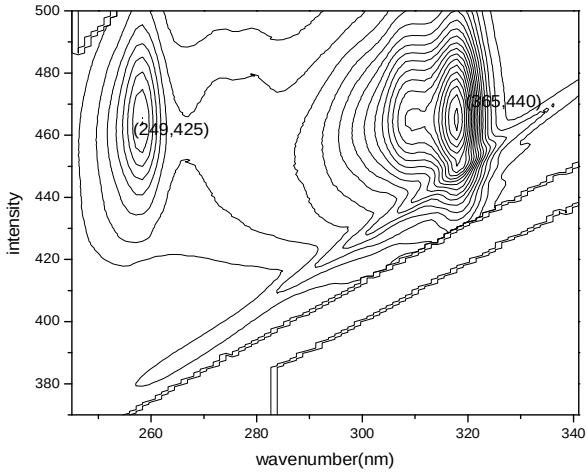


Figure 18:- Contour plot of 2,2'-biquinoline inAcetonitrile solution.

Since excitation spectrum depends on emission wavelength and vice versa, it is possible to identify which excitation band corresponds to the low or higher energy emission band. In acetonitrile, the 3D spectra of 2,2'-biquinoline gives two contour centers (Figure 18). The excitation at λ_{Exc} = 249 nm gives the emission band at λ_{Em} = 425 nm, and the second excitation band at λ_{Exc} = 365 nm corresponds to the emission band at λ_{Em} = 440 nm (Figure 17). The Presence of two contour centers supports explanations given for the existence of two species that absorbs and emits at their own distinct wavelength.

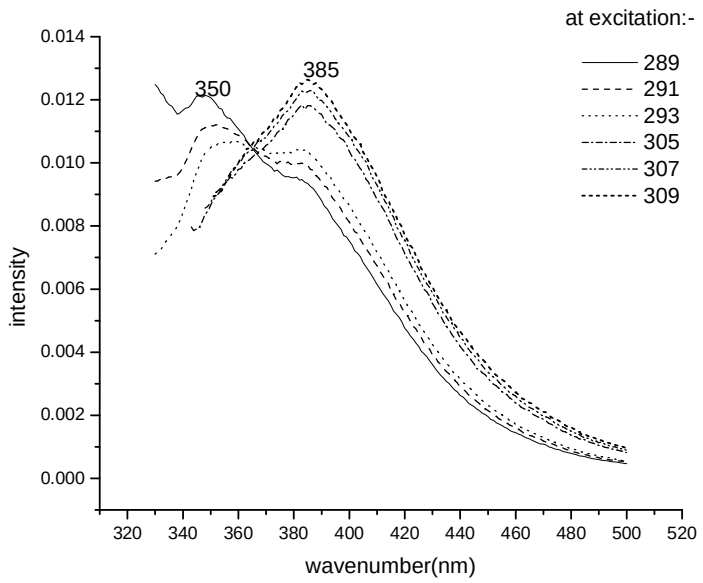


Figure 19: Peak normalized emission spectra of 2,2'-biquinoline in P-dioxane.

In p-dioxane, shown in Figure 19 normalized emission spectra in the wavelength range 289 nm-309 nm gives an isoemissive point centered at 364 nm , indicating two emitting states originating from two equilibrium structures of a molecule in the ground state. For the reason stated above, two different ground state species that fluoresce are responsible for the observed properties.

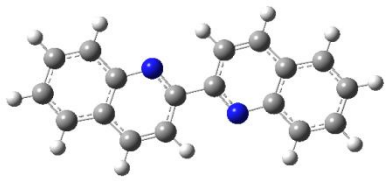
The emission bands were found to be highly dependent on the excitation wavelengths. As the excitation wavelength varied the ratio of the intensity of cis to trans bands changed significantly. This phenomenon is in violation of the kasha rule, which states that for a single electronic transition the band shape of the emission spectrum should stay the same regardless of the excitation wavelength; *i.e.* the emission band intensities (ratio) should not be dependent on the excitation wavelength. Thus, the observed wavelength dependence may indicate the presence of two species in the ground state, as the existence of two electronic transitions may be excluded in the P-dioxane, Acetonitrile and Dichloromethane solvent for trans and cis confermer of 2,2'-biquinoline.

The solvent dependence of the fluorescence spectra clearly shown that the emission wavelength in less polar P-dioxane is blue shifted from acetonitrile and dichloromethane spectra. The emission spectra is red shifted in the case of the more polar acetonitrile and dichloromethane .

For most of compounds, only a single fluorescence band is observed. But it was found that some compounds show more than one fluorescence bands. For these types of compounds, different models were developed to explain this unusual property[29,30]. The types models that exactly explain the observed properties vary from compound to compound. The dual fluorescence of 2,2'-biquinoline (Figure 14-18) may be assigned to the presence in the ground state of two electronically different absorbing species or the different types of processes taking place in the excited state leading to the generation of electronically different chemical species. Conformational isomers eneration in the ground and excited states or in only one of the states is proposed for most of the compounds showing this unusual phenomenon. Formation of conformation isomers in excited states by rotation a group or groups were found to explain well this phenomenon for compounds like DMABN[2-5]. If only single excitation wavelength is responsible for the observed emission bands i.e. if emission spectrum is independent of excitation wavelength, excited state introversion (equilibrium) is responsible for the observed bands[16,29]. But if the emission spectrum shows dependence on excitation wavelength, equilibrium between ground state electronic structures is responsible for the observed bands. Therefore, one can easily identify whether equilibrium between ground state electronic structures or equilibrium between excited state electronic structures are responsible for dual fluorescence by checking the dependence of emission spectra on excitation wavelength and dependence of emission spectra on excitation wavelength. Therefore, the presences of two ground state species, most probably cis/trans conformers, are responsible species for the observed wavelength dependency of the excitation and emission spectra. Since excitation spectrum depends on emission wavelength and vice versa, it is possible to identify which excitation band corresponds to the low or higher energy emission band. Presence of two contour centers in acetonitrile and dichloromethane supports explanations given for the existence of two species that absorbs and emits at their own distinct wavelength. From observations, dual emission is observed in the relatively more polar solvents acetonitrile, dichloromethane and p-dioxane whereas only single emission is observed in an non-polar cyclohexane.

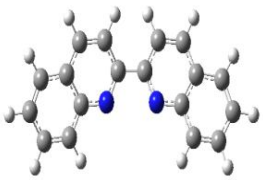
3.2. Computational Investigation of Molecular Properties of 2,2-biquinoline

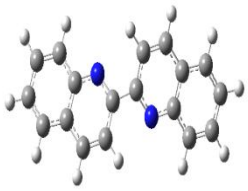
In order to correlate the experimental findings, computational calculations of some photophysical properties of 2,2'-biquinoline were studied. All calculations were performed using the GAUSSIAN03 suite of programs. Ground-state optimizations were performed at the DFT level using the B3LYP functional. Optimization is used to identify the global minimum structures of a given compound. During optimization of 2,2'-biquinoline via DFT/ B3LYP/STO-3G, the global minimum structure (most stable) was found to be the planar (Schem 2).



Scheme 2:- Optimized structure of 2,2'-biquinoline

Optimized ground-state geometries were calculated for both isomeric structures 2,2'-biquinoline of (IA and IIA) are optimized using the semi-empirical of INDO methods without any geometrical restriction except those enforced by symmetry. The optimized geometries were confirmed to be there are two energy minima: cis-like structure with 140^0 twisted out of plane as local minima and the planar trans structure with 30^0 as absolute minima (Scheme 3).

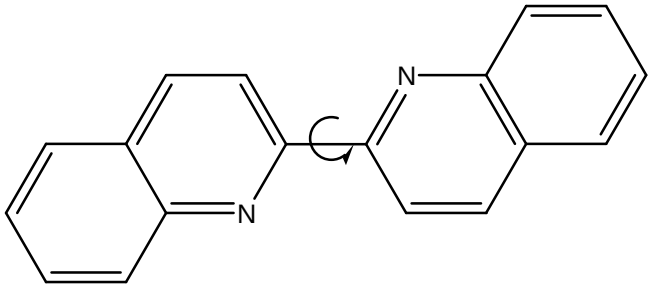




IA **IIA**

Scheme 3: The absolute and local minima of 2,2'-biquinoline IA and IIA

During calculation of the ground-state potential energy surface (PES) of the given compound, 2,2'-biquinoline, structures related by bond rotations usually interconvertible at room temperature. As it was already described 2,2'-biquinoline is among the molecule that is expected to rotate about the bond joining the two rings (C_2 - C'_2) exhibiting a different conformational behavior to that of biphenyl[31]. The presence of the two N atoms in the ortho/ ortho' position relative to thebond joining the rings substantially affects the geometry of this molecule. Energy should be supplied to twist a bond into a specific conformation known as barrier to rotation or torsional energy, which is defined as relative energy difference between highest energy conformer and lowest energy conformer. For 2,2'-biquinoline potential energies were calculated for every 10^0 rotations of the one of quinoline ring as shown in scheme 4.



Scheme 4:- Rotation of the quinoline ring about the C-C' bond.

Scanning of the dihedral angle of quinoline group through rotational angle about NCC'N' to the benzene ring was found to have two minimum in potential energy surface (PES). The PES calculated via semi-empirical of INDO methods, As can be seen in the potential energy curves (Figure19), through absolute minima to local minima, maximum energy was reached when twisting angle about the NCC'N' reaches 90^0, perpendicular configuration of the quinoline rings to each other. There are two energy minima: cis-like structure with 140^0 twisted out of plane as local minima and the planar trans structure as absolute minima.

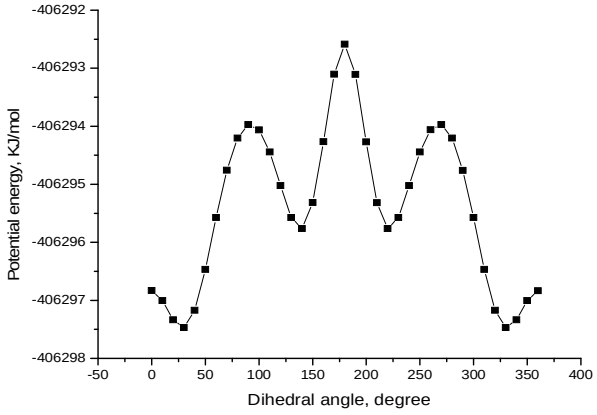
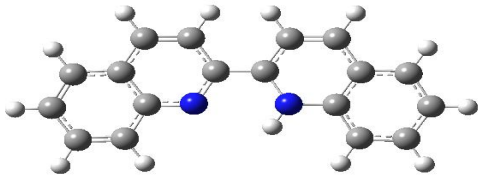


Figure 20:- Rotational angle about NCCN versus ground state potential energy for every10^0 rotation of the quinoline ring using semi-empirical of INDO methods.

For ground state 2,2'-biquinoline, interconversion of cis/trans requires additional energy that overcome the barrier energy (the energy of activation for interchanging to one another) calculated to be 1.775 and 3.524 kJ/mol for cis conformer IA and trns conformer IIA,

respectively. The energy barrier for both conformers is less than the room temperature thermal energy, 3/2R*T* = 3.77KJ/mol, indicating that the two structures coexist at room temperature. Since the rotational barrier is small, they can exist as a mixture. However, if a barrier is large with respect to the thermal energy at room temperature, the conformers may be resolved, but the barrier energy of the trans conformer is comparable with room temperature thermal energy, they coexistence is environment selective. Therefore, this result obtained from theoretical calculation is in good agreement with the experimental results of 2,2'-biquinoline in dichlorometane, further supporting the experimental findings.

The existence of cis and trans structures of 2,2'-biquinoline distinctively in ground state, as the calculated value indicates, supports the suggested justifications given for the causes of the wavelength dependency of emission and excitation spectra observed experimentally. Optimized monoprotonated 2,2'-biquinoline (scheme 5) was found to possess cis structure in which is in agreement with the experimental result .



Scheme 5:- Optimized structure of monoprotonated 2,2'-biquinoline using DFT/B3LYP /STO-3G basis set

The potential energy curve of the monoprotonated 2,2'-biquinoline given in Figure 20 shows two energy minima for cis structure with 0^0 dihedral angle as global minima and the trans structure with 180^0 as local minima on rotational angle about N-C-C`-N.

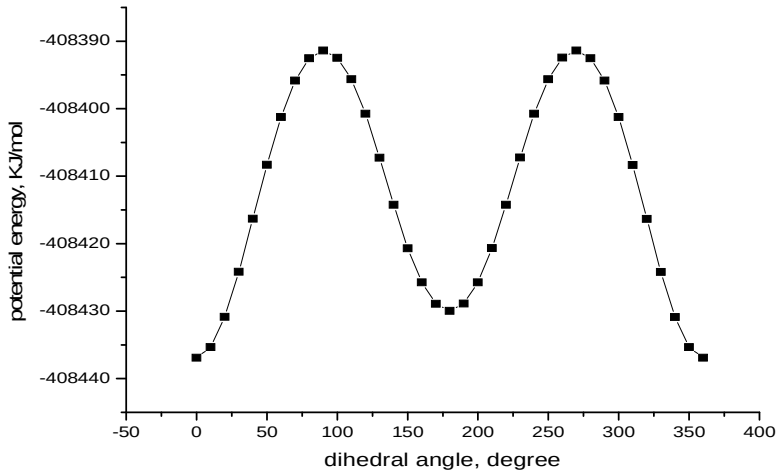


Figure 21:- Rotational angle versus ground state potential energy of mono protonated 2,2'-biquinoline ring using semi-empirical of INDO methods.

The rotational activation energy barrier for monoprotonated 2,2'-biquinoline was calculated to be 47.92 and 38.843 KJ/mol for cis conformer and trans conformer respectively. Table 3 below, shows that ground state energy of the local minima (trans) and absolute minima (cis) of monoprotonated 2,2'-biquinoline of quinoline ring using semi-empirical of INDO methods.

Table 3

Rotational barrier (KJ/mol)	ΔEcis-trans (kJ/mol)
47.92	9.1

For biprotonated 2,2'-biquinoline, even higher barrier energy but very low energy difference between the cis and trans structure was found with trans conformer being at the absolute minima. Thus, comparison of the present experimental and computational studies of 2,2'-biquinoline indicates that the gradual changes observed in the band shape and position by varying pH, Zn^{2+} ion and excitation or emission wavelength can be attributed to the presence of cis/trans isomeric structures.

4. SUMMARY AND CONCLUSION

Absorption spectra show small shift in solvents of different polarity indicating small difference between the dipole moments of the Franc-Condon (FC) excited state and the ground state and suggests a small degree of charge transfer in the FC excited state.

Upon increasing emission wavelength in dichloromethane and acetonitrial solvents in excitation spectra, the intensity of the higher energy band diminishes and new band at the lower energy edge appears signifying presence of two ground state species emitting at different wavelength.

Two distinct emission spectra were observed upon progressive increase in excitation wavelengths in dichloromethane, acetonitrile and p-dioxane solvents producing more red shifted spectra in dichloromethane and acetonitrile. In both acetonitrial and dichloromethane solvents the presence of two emitting species was supported by contour plot showing the correspondence between emission and excitation spectra. The analysis made show that the spectral changes related to wavelength dependency is due to the presence of two ground state equilibrium species (cis/trans isomers) that absorbs and emits photon of specific energy

Stepwise addition of metal ions, Zn^{2+}, made possible the assignment of the shorter wavelength of absorption and emission band as originated from trans and the longer wavelength band to cis conformer. Up on addition of proton on the absorption spectra of 2,2'-biquinoline were similar to that of the metal ions for different pH values but the band in the absorption spectra was more broad than the band absorbed form metal ion.

Computational results predict the presence of two low energy conformers of 2,2'-biquinoline to be the cis-like (relatively less stable) structure and trans (more stable) structure. In contrast, cis structure is more stable in acidic media than the trans structure.

These results, dependency of emission spectrum on the wavelength of exciting light, the existence of two excitation bands, together with the presence of one isoemissive point, and the observation of two minima's for the optimized ground state PES calculation can only be 2,2'-biquinoline explained by the presence of two relatively stable ground state conformers of the compound in equilibrium, exciting at different wavelength and emitting at their corresponding wavelengths.

Therefore, the origin of the spectral changes observed are due to the presence of ground state cis/trans conformers and their population changes in the presence of metal ions and pH of the solution. Progressive change in excitation wavelength, metal ion concentration and shows change in the fluorescence excitation spectra.

4. Referance

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