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Computational Study on Hydrogen Bonded Complexes formed by Anthyridone and 2,6-diaminopyridine-3,5-dialdehyde and their Derivatives

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ADDIS ABABA UNIVERSITY
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DEPARTEMENT OF CHEMISTRY

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Declaration

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

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

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Abstract

Computational study was performed on a hydrogen bonded complex formed by antyridone and 2,6-diaminopyridine-3,5-dialdehyde. Six other complexes were designed based on the structure of the complex by changing the R- group of monomer A in to C_6H_5, p-toluene, p-phenol, OH and OCH_3, the X group of monomer B in to chlorine. The binding energies of the complexes were calculated based on their optimized geometry using DFT/B3LYP at 6-31 G level. The electronic spectra for the complexes were calculated with ZINDO and IR spectra of the monomers and complex 1 were computed using DFT/B3LYP at 6-31 G level. It was indicated that all complexes could be formed, via hydrogen bonds. Complexes 2 - 4 were hindered due to steric effect. Electron donating nature was the stability factor. The first absorptions in the electronic spectra of the complexes were red shifted compared with those of the monomers. The stretching vibrations of the N – H bonds were increased with the formation of the hydrogen bond.

Key Words: antyridone, 2,6-diaminopyridine-3,5-dialdehyde, DFT and hydrogen bond

1. Introduction

The importance of intermolecular interaction in biology and material science has prompted chemists to explore the nature of the variety of such interactions. The strongest of these interactions are the hydrogen bonds, which play an important role in determining the molecular conformation, crystal packing, and the structure of biological systems such as nucleic acids [1]. It plays an important role in nature, especially in the biological materials and of processes related to DNA and drug design. Thus hydrogen bonding is applied in many ways such as synthesis of polymers, self assembly of functional material, drug design and crystal engineering [2].

Extensive experimental and theoretical efforts have been devoted to the studies of these interactions, such as C-H ……0, C-H …II and H ….H hydrogen bonds[1]. Hydrogen bonding between water and a series of small organic molecules was examined using a hybrid density functional procedure (B3LYP) and second-order Møller Plesset theory (MP2) coupled with a double ζ basis set [3]. *Ab initio* quantum mechanical calculations at the MP2 level were used for an extensive study concerning the stability of hydrogen bonded complexes formed by pyrrole and thiopene, which are the most common building blocks of conducting polymers, and DNA bases [4].The hydrogen bonding interaction of 1:1 dimmers formed between HNO and HArF molecule investigated using second order Møller Plesset perturbation (MP2) method in conjunction with 6-311*G**, 6-311 ++ G** and 6-311++G(2d,2p) basis sets [5].

In the earliest work the hydrogen bonded complexes formed by the anthyridone and dialdehyde derivatives were computationally studied using semi empirical methods at AM1 level. The binding energy of the complexes and their IR spectra were calculated using AM1 method. The electronic spectra were also computed using INDO / CIS method [6].

In this study the properties of the hydrogen bonded complexes formed by the anthyridone and 2,6-diaminopyridine-3,5-dialdehyde and their derivatives were computed. The binding energy of the complexes and their electronic nature at the ground state were calculated using density functional theory (DFT) with B3LYP/6-31G (7d, 6f) level. Also their electronic absorption spectra were investigated theoretically with ZINDO and TD/B3LYP/6-31G (7d, 6f) level. Finally, IR frequencies of monomers A, B and complex 1 are calculated utilizing B3LYP/6-31G (7d, 6f) level.

2. Computational Chemistry

Modern science utilizes four basic approaches to the study of how nature works: observational science, experimental science, theoretical science, and computational science. Of these four, computational science is the newest, made possible by the tremendous improvements in both computer hardware and software. Computational science, sometimes known as modeling and simulation or scientific computing, is used extensively in chemistry, and is known as computational chemistry or molecular modeling. Molecular modeling is the general term used to describe the use of computers to construct molecules and perform a variety of calculations on these molecules in order to predict their chemical characteristics and behavior.

Computational chemistry is a standard tool of science which usually used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer. It simulates chemical structures and reactions numerically, based on in full or inpart on the fundamental laws of physics and allow chemists to study chemical phenomena by running calculations on computers rather than by examining reactions and compounds experimentally. It is used to calculate chemical structure (number and type of atoms, bonds, bond lengths, angles, and dihedral angles);its properties (basic characteristics of the molecule, such as its molecular energy, enthalpy, and vibrational frequencies); and its activity (those characteristics that describe how the molecule behaves in the presence of other molecules, such as its nucleophilicity, electrophilicity, andelectrostatic potentials). Computational chemistry is therefore both an independent research area and a vital adjunct to experimental studies.

Basically there are two broad ways with in computational chemistry devoted to calculate the structure of molecules and their reactivity: molecular mechanics and electronic structure methods [7].

2.1. Computational methods

2.1.1. Molecular mechanics

Molecular mechanics, or force field, simulations use the laws of classical physics to predict structures and properties of molecules. It is the application of classical mechanics to molecules. Classical mechanics is used to describe the motion of macroscopic objects. In molecular mechanics, atoms are treated as spheres whose mass depends on the element. Chemical bonds are treated as springs whose stiffness depends on which elements are bound together, and whether the bond is single, double, or triple. Other types of springs are used to model changes in bond angles, dihedral angles, etc. Each of these various types of springs will have spring constants associated with them. It set up a simple algebric expression for the total energy of a compound with no necessity to compute a wave function or total electron density. The energy expression consists of simple classical equations, such as the harmonic oscillator equation in order to describe the energy associated with bond stretching, bending, rotation and intermolecular forces, such as Vander walls interactions and hydrogen bonding. All of the constants in this equation must be obtained form experimental data or an *ab initio* calculation.

A set of equations with their associated constants is called force field. Modern force fields contain many more types of potential function designed to give a good fit to the experimental data. The most important of these additional functions are the torsional potentials. A further important advance was made with the inclusion of one- and two fold torsional functions in the MM2 force field. This gave a dramatic improvement in the results for some molecules. The combination of bond-stretching, angle-bending, and torsional potential function is often known as a valance force field because it accounts for the properties normally attributed to chemical bonds.

The fundamental assumption of the molecular mechanics method is the transferability of parameters. This means that a given type of bond, for instance, is assumed to have the same characteristics in each molecules in which it occurs. That is often a good approximation shown by the success of molecular mechanics calculation.

The first step in the molecular mechanics calculation is determination of the interatomic distance, bond angles in starting geometry. The values obtained are then used in the different potential function expressions to calculate an initial steric energy, which is simply the sum of the various potential energies calculated for all the bonds, bond angles, non bonded pairs of atoms and so forth in the molecule. It is important to note that this steric energy is specific to the force field. It does not correspond to any classical definition of strain energy, although it is related to the heat of formation by a simpler expression. Because all other factors remain constant through out the optimization of a structure it is enough to find a minimum with respect to the steric energy [8].

2.1.2. Electronic structure methods.

Methods aimed at solving the electronic Schrödinger equation are broadly referred to as electronic structure calculation. Electronic structure methods use the laws of quantum mechanics rather than classical physics as the basis for their computations. Quantum mechanics states that the energy and other related properties of a molecule may be obtained by solving the Schrödinger equation.

$$H\Psi = E\,\Psi \qquad [2.1]$$

Where, H is energy operator which describes the kinetic and potential energy of an electron in field of nuclear and other electrons. Ψ is a set of spatial distributions describing the probability of finding electrons. E is the sum of the energies of the orbital.

Electronic structure methods differ mainly according to how, or if, electron correlations is treated. Electron correlation is the tendency of electrons to avoid each other, even with in the same orbital.

The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular Schrödinger equation associated with the molecular Hamiltonian. Methods that do not include any empirical or semi-empirical parameters in their equations being derived directly from theoretical principles, with no inclusion of experimental data are called *ab initio* methods. Semi-empirical quantum chemistry methods make many approximations and obtain some parameters from empirical or experimental data [9].

A. *Ab initio* methods

The most common type of *ab initio* calculation is called a Hartee- Fock calculation, in which the primary approximation is the central field approximation. This means that the coulombic electron-electron repulsion is taken into account by integrating the repulsion term. This gives the average effect of the repulsion, but not the explicit repulsion interaction. This is a variation calculation, meaning that the approximate energies calculated are all equal to or grater than the exact energy.

In Hartree- Fock method electron correlation is ignored. This means that HF takes into account the average affect of electron repulsion, but not the explicit electron interaction. This method breaks the many-electron Schrödinger equation in to many simpler one- electron equations. Each one electron equation is solved to void a single-electron wave function, called an orbital energy. The orbital describes the behavior of an electron in the net field of all the other electrons. The many electron wave function (Ψ) is estimated by the self-consistent field (SCF) with an initial guess of Ψ (Ψ_0); which is the product of the initial estimates of the molecular orbitals.

$$\Psi_0 = \Psi_0(1)\,\Psi_0(2) \qquad [2.2]$$

Then, while all other MO functions are held constants each Ψo is varied so as to minimize the total energy. This is the variational method. This gives a new Ψ (Ψ_1).

$$\Psi_1 = \Psi_1(1)\,\Psi_1(2) \qquad [2.3]$$

This procedure continues iteratively until the energies and orbital coefficients remain constant from one iteration to the next. This is called having the calculation converge. This iterative procedure is called a self- consistent field procedure (SCF) [10].

A variation on the HF procedure is the ways that orbitals are constructed to reflect paired or unpaired electrons. If the molecule has a singlet spin, then the same orbital spatial function can be used for both ά and β spin electrons in each pair. This is called the restricted Hartree-Fock method (RHF).There are two techniques for constructing HF wave functions of molecules with unpaired electrons. One technique is to use two completely separate sets of orbital for the ά and β electrons. This is called an unrestricted Hartree-Fock wave function (UHF).This means that paired electrons will not have the same spatial distribution. Another way of constructing wave function for open-shell molecules is the restricted open shell Hartree-Fock method (ROHF).In this method, the paired electrons share the same spatial orbital; thus there is no spin contamination [11].

Hartree-Fock, or SCF methods, therefore, does not include electron correlation. This limitation is being addressed with the development of newer, “post-SCF” methods that do attempt to take into account electron correlation.

Møller- Plessent perturbation theory (MPn, where n is the order of correction) is another *ab initio* method which can be used to correct for correlation. Correlation can be added as a perturbation from the HF wave function. Electron correlation is accounted for allowing one or more electrons to occupy higher energy, unoccupied MO’s. This results in an energy correction that lowers the total energy because it lowers the electron- electron repulsion energy.

The commonly used MP2 method actually considers the effect of 2 electrons occupying anti-bonding orbital. Third order (MP3) and fourth order (MP4) calculations are also common. MP2 is more expensive than HF because more configurations must be calculated [12].

B. Density functional Theory

Density functional theory (DFT) methods are often considered to be *ab initio* methods for determining the molecular electronic structure, even though many of the most common functional use parameters derived from empirical data, or from more complex calculation. In DFT, the total energy is expressed in terms of the total electron density rather than the wave function. It is an alternative approach, which uses general functional of the electron density to model exchange and correlation energies [13].

DFT was developed by Walter Kohn and others and put on a firm theoretical footing when Hohenberg- kohn theorems was established. The first theorem demonstrates the existence of a one-to-one mapping between the ground state electron density and the ground state wave function of a many-particle system. Further, the second HK theorem proves that the ground state density minimizes the total electronic energy of the system.

The predecessor to density functional theory was the Thomas-Fermi model, developed by Thomas and Fermi in 1927. They calculated the energy of an atom by representing its kinetic energy as a functional of the electron density, combining this with the classical expressions for the nuclear-electron and electron-electron interactions.

Although this was an important first step, the Thomas-Fermi equations accuracy was limited because it did not attempt to represent the exchange energy of an atom predicted by Hartee-Fock theory. Exchange energy functional was added by Dirac in 1928. In many-body electronic structure calculations the nuclei of the treated molecules or clusters are seem fixed, generating a static external potential V in which the electrons are moving. A Stationary electronic state is then described by a wave function $\Psi(\vec{r}_1,...,\vec{r}_N)$ fulfilling the many electron Schrödinger equation

$$H \Psi = [T+U+V] \Psi$$

$$= \left[\sum_{i}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i}^{N} V(\vec{r}_i) + \sum_{i<j} U(r\vec{i}.r\vec{j}) \right]\Psi$$

$$= E\,\Psi \qquad [2.4]$$

Where H is the electronic molecular Hamiltonian, N is the number of electron & Ψ is the electron-electron interaction. The operators T and U are so-called universal operators as they are the same for any system, while V is system dependent. There are many sophisticated methods for solving the many – body Schrödinger equation based on the expansion of the wave function in Slater determinant. While the simplest one is the Hartree-Fock method, more sophisticated approaches are usually categorized as post Harfree-Fock Methods.

DFT provides an appealing alternative; being much more versatile as it provides a way to systematically map the many-body problem, with U, on to a single-body problem with out U. In DFT the key variable is the particle density n ($\vec{r}$) which is given by

$$n(\vec{r}) = N\int d^3r_2 \int d^3r_3 ... \int d^3r_N \Psi^*(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) \qquad [2.5]$$

Hohenberg and kohn proved in 1964 that the relation expressed above can be reversed i.e. to a given ground state density $n_o(\vec{r}\,)$ and it is in principle possible to calculate the corresponding ground state wave function $\Psi o(\vec{r}_1,...,\vec{r}_N)$. In other words, Ψo is a unique functional of n_o i.e.

$$\Psi o = \Psi o[n_o] \qquad [2.6]$$

In particular, the ground state energy is a functional of n_o.

$E_o = E\,[n_o]$

$$= \left\langle \Psi\, o[n_o] \middle| T + U + V \middle| \Psi o[n_o] \right\rangle \qquad [2.7]$$

Where the contribution of the external potential < Ψ_0 [n_o] / v / Ψ_0 [n_o]> can be written explicitly in terms of the density.

$$V\,[n] = \int V(\vec{r})n(\vec{r})d^3r \qquad [2.8]$$

The functionals T [n] and U [n] are called universal functional while V [n] is obviously non-universal, as it depends on the system under study. Having specified a system, i.e. V is known, one then has to minimize the functional.

$$E[n] = T[n] + U[n] + \int V(r)\, n(r)\, d^3{}_r \qquad [2.9]$$

With respect to n ($\vec{r}$), assuming one has got reliable expressions for T [n] and U [n]. A successful minimization of the energy functional will yield the ground state density n_o and thus all other ground state observables [9].

C. Semi-empirical methods

Semi- empirical calculations are set up with the same general structure as a HF calculation in that they have a Hamiltonian and a wave function but make many approximations and obtain some parameters from empirical data. The central assumption of semi empirical methods is the zero differentials over lap (ZDO) approximation which neglects all products of basic functions depending on the same electron coordinates when located on different atoms.

The earlier semi-empirical MO methods, CNDO, INDO, and NDDO, were developed by J.a. Pople and his group at a time when the available computers were able to handle *ab initio* calculations only on the smallest systems. The complete neglect of differential overlap (CNDO) method is the simplest of the neglect of differential overlap (NDO) methods. This method models valance orbitals only using a minimal basis set of Slater type orbitals. Practically all CNDO calculations are actually performed using the CNDO/2 method, which is an improved parameterization over the original CNDO/1 method. There is a CNDO/S method that is parameterized to reproduce electronic spectra. The CNDO/S method that is does yield improved prediction of excitation energies, but at the expense of the poorer prediction of molecular geometry The modified neglect of diatomic overlap (MNDO) method is another semi-empirical method that has been found to give reasonable qualitative results for many organic systems. The MNDO, AM1, and PM3 methods are parameterization of the NDDO model, where the parameterization is in terms of atomic variables, i.e. referring only to the nature of a single atom. MNDO, AM1 and PM3 are derived from the same basic approximations (NDDO), and differ only in the way the core –core repulsion is treated , and how the parameters increases as the square of the number of elements..

The Zerner's INDO method (ZINDO) is also called spectroscopic INDO (INDO/S). This is a reparameterization of the INDO method specifically for the purpose of reproducing electronic spectra results. This method has been found to be useful for predicting electronic spectra.

Semi-empirical methods may only be used for systems where parameters have been developed for all of their component atoms. In addition to this, semi-empirical models have a number of well-known limitations. Types of problems on which they do not perform well include hydrogen bonding, transition structures, and molecules containing atoms for which they are poorly parameterized, and so on [11, 14].

2.2. Basis Sets.

Basis sets are a series of numbers that are used by the computational chemistry software to begin the process of describing where the electrons are in proximity to the nucleus and to each other. Specifically, basis sets describe where the electrons are in the atomic orbital.

A basis set in chemistry is a set of functions used to create the molecular orbital which, are expanded as a linear combination of such functions with the coefficients to be delimited. Usually these functions are atomic orbital in that they are centered on atoms, but functions centered in bonds or lone pairs, and pairs of functions centered in the two lobes of a p orbital, have been used. It represents a series of beginning numbers that help the computational chemistry software begin the process of calculating the wave function. The wave function is a mathematical description of where an electron or group of electrons is in relation to the nucleus and to each other. The wave function represents a mathematical approximation at best, but determining the wave function correlates well to the calculation of many atomic and molecular properties. The square of the wave function, calculated over all of the places where the electron is likely to be, gives us the probability of finding the electron or electrons. The knowledge of that probability is directly translatable into properties such as the energy of the molecule and other characteristics.

There are two types of basis functions (also called atomic orbitals) commonly used in electronic structure calculations: Slater Type Orbitals (STO) and Gaussian Type Orbitals (GTO) [15].

$$\text{STO} = \left(\frac{\xi^3}{\pi}\right)^{1/2} e^{-\xi r} \qquad [2, 10]$$

GTO = $(\frac{2\alpha}{\pi})^{3/4} e^{-\alpha r^2}$ [2,11]

Where ζ and α are numbers which can be substituted for each type of basis sets.

In modern computational chemistry quantum chemical calculations are typically performed with in a finite set basis functions. When molecular calculations are performed, it is common to use a basis composed of a finite number of atomic orbitals, centered at each atomic nucleus with in the molecule. Initially these atomic orbital exponentially decay with distance from the nuclei. later were typically Slater orbitals, which corresponded to a set of functions which decayed exponentially with distance from the nuclei. Later, it was realized by Frank Boys that these Slater type orbitals could in turn be approximated as linear combinations of Gaussian orbitals instead. There are hundreds of basis sets composed of Gaussian-type orbitals (GTOS).

The smallest of these are called minimal basis sets and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom.

The most common addition to minimal basis sets is probably the addition of polarizations functions, denoted by an asterisk,*.Two asterisks, **, indicate that polarization functions are also added to light atoms. Another common addition to basis sets is the addition of diffuse functions, denoted in Pople –type sets by a plus sign,+, and in Dunning-type sets by “aug’. Two plus signs indicate that diffuse functions are also added to light atoms [16].

2.2.1. Minimal basis set.

The most common minimal basis set is STO-nG, where n is an integer. This n Value represents the number of Gaussian primitive functions comprising a single basis function. In these basis sets, the same number of Gaussian primitives comprise core and valence orbitals .Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper than their larger counter parts. Minimal basis sets contain the minimum number of basis functions that are needed for each atom. The major problems with the minimal basis set family (STO-nG), is that it considers all electrons to be equal.

Minimal basis sets use fixed size atomic type orbitals. Commonly used minimal basis sets are;- STO – 3G, STO – 4G, STO – 6G, STO – 3G*. Etc.

2.2.2. Split Valence basis sets.

The notation for the split valance basis sets arising from the group John - Pople is typically X-YZg. In this case X represents the number of primitive Gaussians comprising each core atomic orbital basis function .The Y and Z indicate that the valance orbital are composed of two basis functions each, the first one composed of a linear combination of Y primitive Gaussiain function, the other composed of a linear combination of a primitive Gaussian function.

Commonly used split-valence basis sets are;-3 – 21 G, 3 – 21 G*, 3 – 21 + G, 6 – 31 G, 6 – 31 G* etc

2.2.3 Multiple Zeta Basis Sets

Basis sets in which there are multiple basic functions corresponding to each valence atomic orbital are called valence double triple quadruple zeta----, basis sets. They are the most widely used basis sets which developed by Dunning and coworkers. The basis sets are named as follows cc-pVNZ where N=D, T, Q, 5, 6… (D=doublet, T= triplet…etc)[14].

3. Objectives and Computational Details

3.1. Objectives

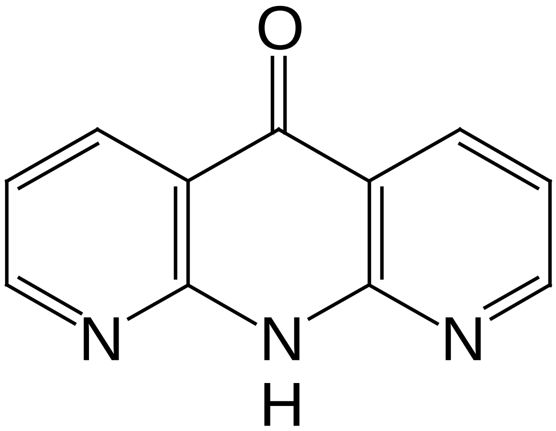
The major objectives of this research project are:

1. to determine the formation of hydrogen bonded complexes
2. to identify the stable hydrogen bonded complexes

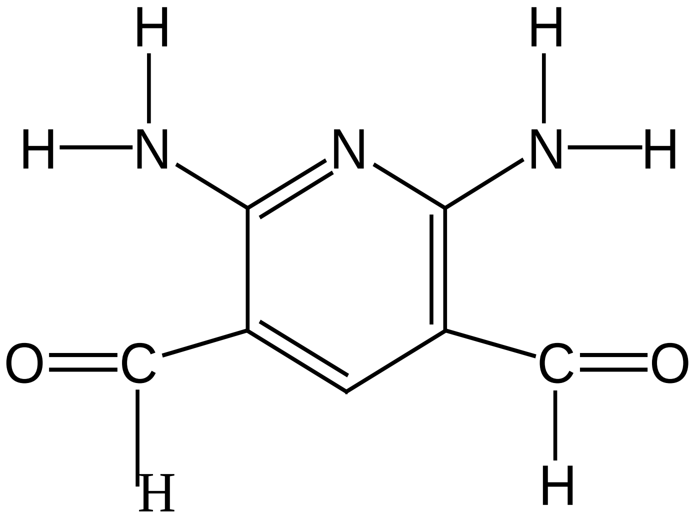
3.2 Computational Details

Hydrogen bonded dimmer was composed of anthyridone (Monomer A) and 2, 6-diaminopyridine-3, 5-dialdehyde (Monomer B).The structure of the monomers are given below.

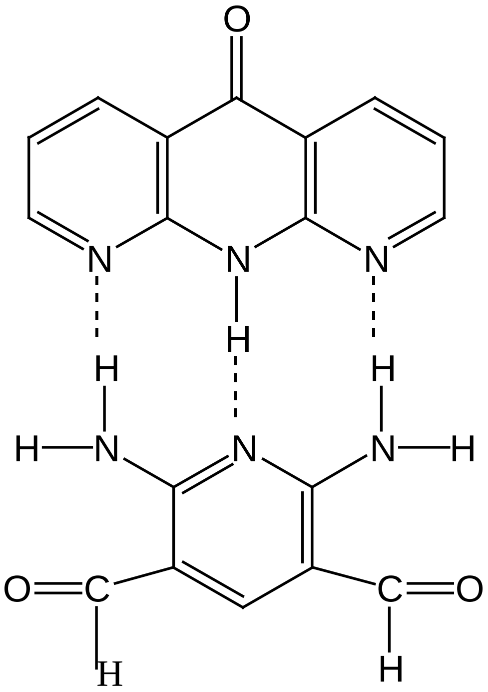
Monomer A: Anthyridone



Monomer B: 2, 6-diaminopyridine-3, 5-dialdehyde



The structure of complex 1 which was made by triple hydrogen bond between anthyridone and 2,6-diaminopyridine-3,5-dialdehyde



Based on the above structure six other possible complexes were formed as follows, by varying R and X

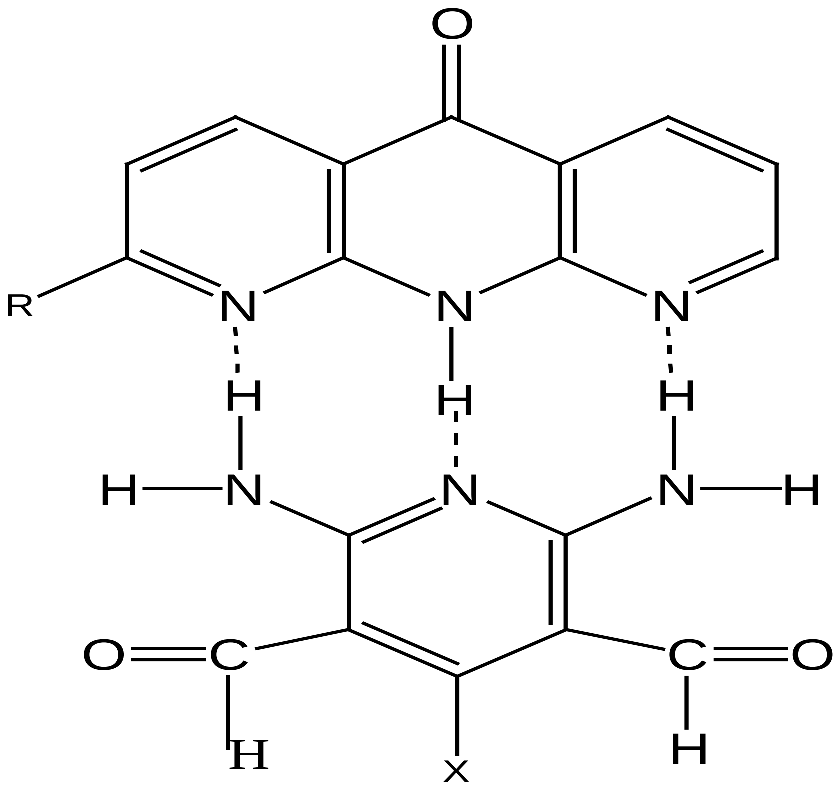


Table 1: The structure of the complexes

Complex	R	X
2	$-C_6H_5$	H
3	p-toluene	H
4	p-phenol	H
5	OH	H
6	OCH_3	H
7	H	F

Geometries of the studied compounds were optimized using B3LYP with 6-31G basis sets, which are known to yield good geometry parameters at a moderate computational cost [15]. Binding energy and IR spectra of the complexes were determined using optimized geometry of the complexes by DFT/ B3LYP with 6-31G (7d, 6f) basis sets. The binding energy was computed as the difference between the sum of the monomers energy and the total energy of the complex. The binding energy was corrected with the zero point energy calculated at DFT. Frequencies computed were also scaled to eliminate known errors. The electronic natures of the complexes at the ground state, the HOMO – LUMO energy and energy gap, of the complexes were calculated by DFT/B3LYP at 6-31G (7d, 6f).

Electronic spectra of the monomers and complexes were calculated using ZINDO and TD/B3LY P/6-31G levels. The Gaussian 03 package of programs was used for all calculations [16]

4. Result and Discussion

4.1 Optimized structures, Binding energy and stability of the complexes

From optimized structures of monomer A, Monomer B and complex 1 the following important results were obtained using DFT/B3LYP at 6-31G (7d, 6f).

Table 2: Charge of the elements of monomer A

Element	Charge
C[1]	-0.024
C[2]	0.184
C[3]	-0.184
C[4]	1.018
C[5]	-0.890
N[6]	-0.147
C[7]	0.045
C[8]	1.018
O[9]	-0.549
C[10]	-0.890
N[11]	-0.611
H[12]	0.321
C[13]	-0.184
C[14]	-0.024
C[15]	0.184
N[16]	-0.147
H[17]	0.133
H[18]	0.138
H[19]	0.133
H[20]	0.138
H[21]	0.168
H[22]	0.168

The following atoms are responsible for the formation of hydrogen bond

N [6] = -0.147

H [12] = 0.321

N [16] = -0.147

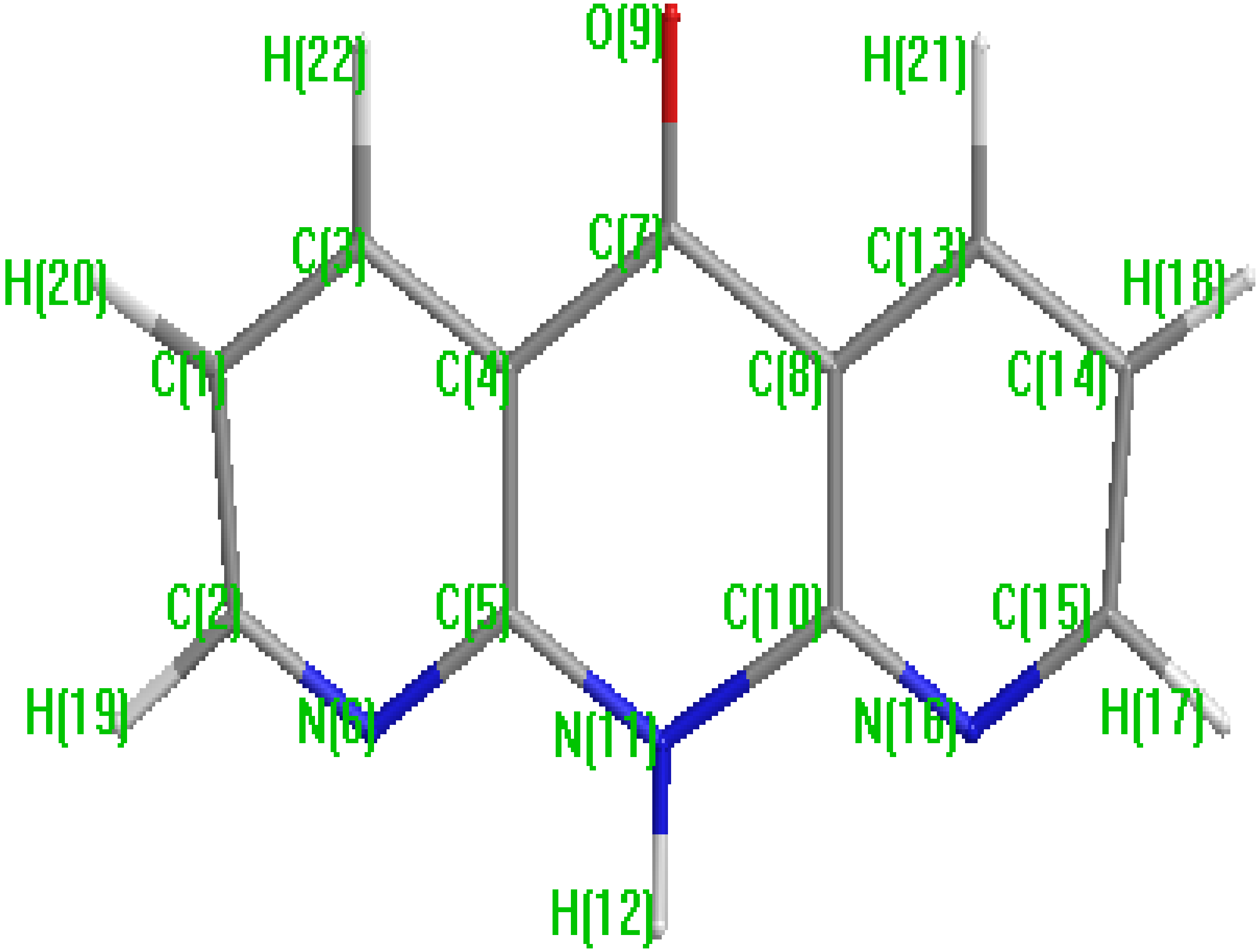


Figure 1: Optimized geometry of monomer A

Table 3: Charge of the elements of monomer B

Element	Charge
N[1]	-0.495
C[2]	0.396
C[3]	0.396
C[4]	0.031
C[5]	0.031
C[6]	0.180
N[7]	-0.727
N[8]	-0.727
C[9]	0.182
C[10]	0.182
H[11]	0.321
H[12]	0.373
H[13]	0.321
H[14]	0.373
O[15]	-0.482
H[16]	0.159
O[17]	-0.452
H[18]	0.159

The following atoms are responsible for the formation of hydrogen bond

H [11] = 0.321

N [1] = -0.495

H [13] = 0.321

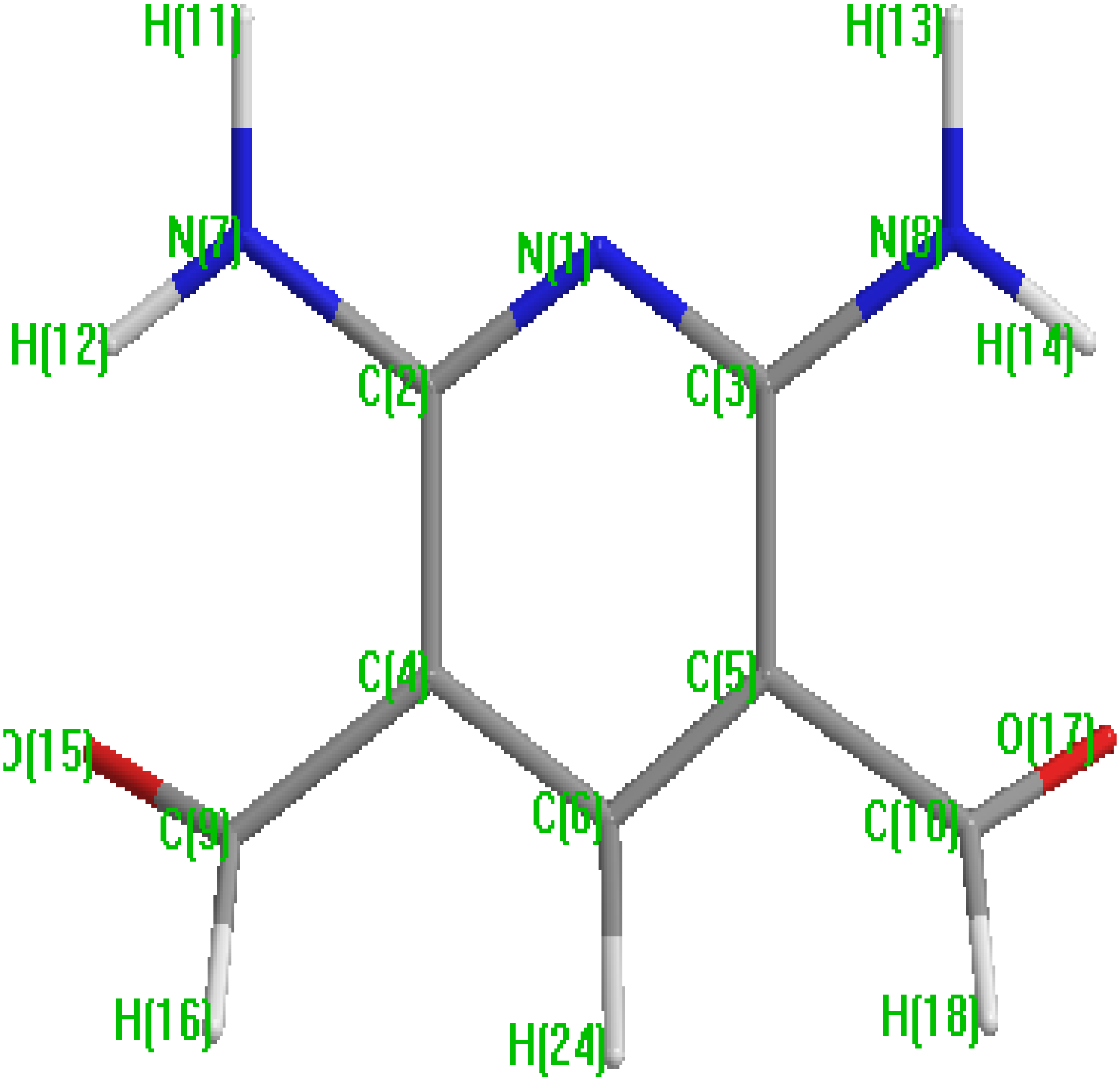


Figure 2: Optimized geometry of Monomer B

Table 4: Bond length of the hydrogen bonds in angstrom obtained from optimized geometry of complex 1

Hydrogen bond	AM1[6]	B3LYP/6-31G
N [21] … H [36]	2.693	2.243
N [29] … H [10]	2.532	2.351
N [19] ... H [34]	2.572	2.263

The bond lengths of the hydrogen bonds in complex 1 calculated by B3LYP/6-31G were 2.243, 2.351 and 2.263 Å for N [21] … H [36], N [29] … H [10] and N [19] ... H [34] respectively.

The N [30] - H [36], N [20] – H [10] and N [31] – H [34] bond length calculated by B3LYP/6-31G are 1.009, 1.028 and 1.012 Å respectively, which are single bonds, and they are shorter than the hydrogen bonds. The bond lengths show clear difference between N – H single bond and N … H hydrogen bond. The hydrogen bond lengths are in consistent with experimental result (2.484Ǻ [6]).

The charges of monomer A and B, which are the possible site for the formation of hydrogen bonds, indicates that through DAD – ADA (D: donor, A: acceptor) triple hydrogen bonded complexes are likely to be formed.

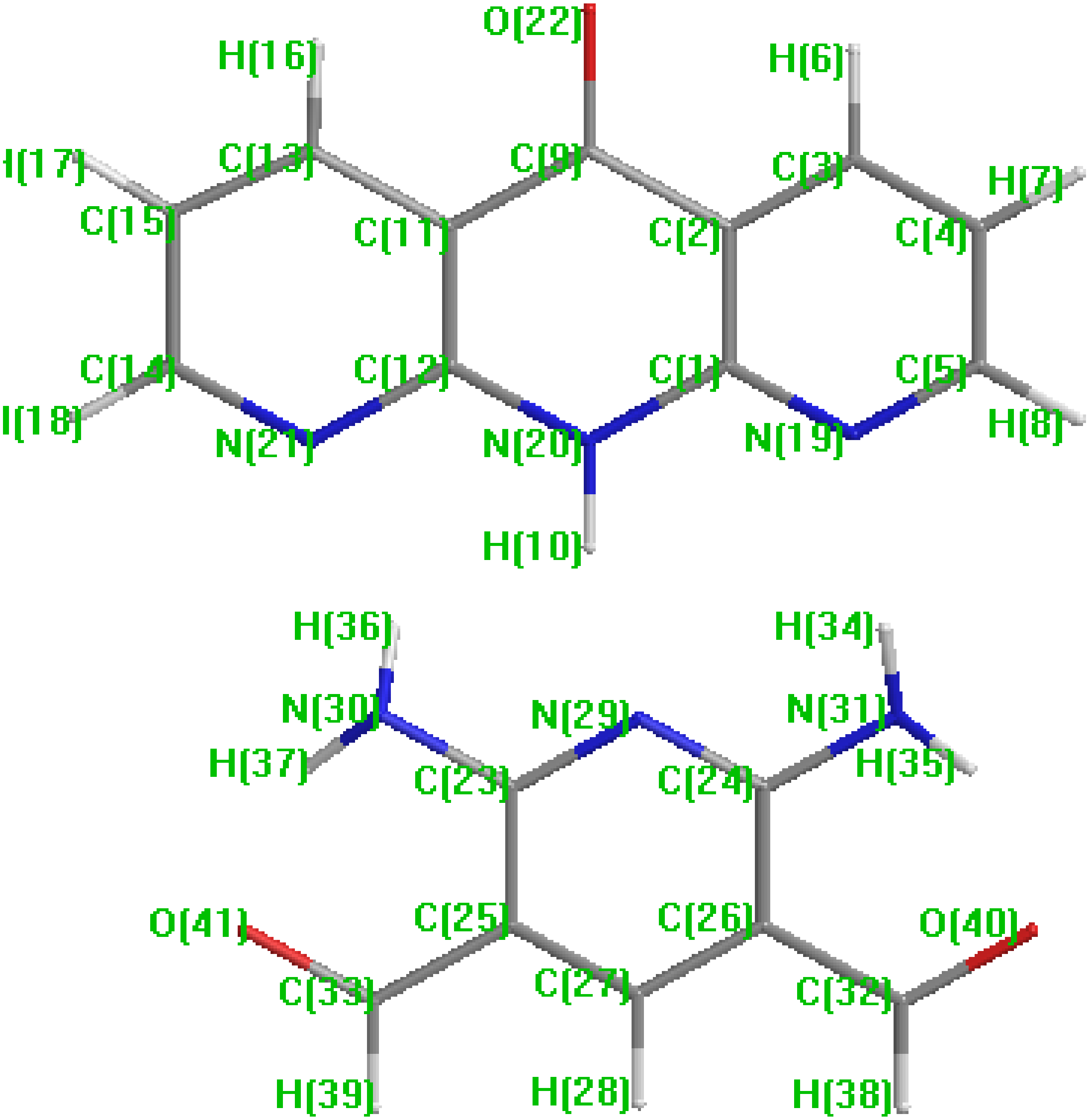


Figure 3: Optimized geometry of complex 1

The binding energy (ΔE) was computed as the difference between the total energy of the complex ($E\,(A\text{-}B)_{AB}$) and the sum of the subsystem energy ($E\,(A)_{AB} + E\,(B)_{AB}$):

$$\Delta E = (E\,(A\text{-}B)_{AB}) - (E\,(A)_{AB} + E\,(B)_{AB})\ [1] \qquad [4.1]$$

The binding energy of the complexes 1 – 7 are given in Table 5. The binding energy of all complexes was negative, which refers that they are able to be formed through hydrogen bond. The stability of the complexes was differing from each other due to structural difference. The less stability of complexes 2 - 4 were because of the steric group attached to monomer A, which hinders the formation of hydrogen bond. Complex 5 and 6 were more stable than complexes 2 – 4 because of electron donating nature of groups on monomer A of complexes 5 and 6.Complex 7 was stable due to the existence of fluorine attached to monomer B, which causes a negative inductive effect on hydrogen.

Table 5: Binding energy of the complexes in Kj/mol

Complex	AM1[6]	B3LYP/6-31G
1	-11.94	-38.58
2	-9.74	-29.63
3	-9.83	-27.85
4	-11.83	-29.74
5	-17.23	-68.56
6	-17.71	-72.84
7	-13.28	-53.76

4.2 The electronic structure at the ground state

The energy gap of complex 1 was 3.08eV less than those of monomer A 3.41eV and monomer B 4.01eV due to the change in the electronic property in complex 1. The energy gap of complexes 2 – 6 were decreased due to electron donating nature of the substituents and that of complex 7 was enhanced because of the electron- withdrawing nature of fluorine.

Table 6: The HOMO – LUMO energy and energy gap of the complexes

Complex	LUMO	HOMO	Energy gap
1	-0.10483	-0.21803	0.11320
2	-0.09094	-0.22608	0.03514
3	-0.17860	-0.21899	0.04039
4	-0.17619	-0.21575	0.04103
5	-0.17883	-0.22173	0.04290
6	-0.17696	-0.22020	0.04324
7	-0.10775	-0.21375	0.10600

Table 7: Energy gap of the complexes in eV

Complex	AM1[6]	B3LYP/6-31G
1	7.90	3.08
2	7.70	0.96
3	7.69	1.11
4	7.68	1.11
5	7.65	1.16
6	7.67	1.17
7	7.80	2.8

4.3 The electronic absorption spectra

The first absorption peak of complex 1 were appeared at 529.52 nm while using ZINDO and 660.77 with TD/B3LYP/6-31G basis set level. Both values indicate that, even if the former is lower than the later, it was red – shifted compared with the monomers, due to its less LUMO – HOMO energy gap. The energy gap of monomer A and complex 1 were 3.3485 and 1.5533 eV respectively. The first absorption peak of complex 2 was lower than complex 1, where as, the complex 3 was higher than both. The first absorption peak of complex 7 was red – shifted than complex 2 – 6 due to fluorine attached at monomer B.

Table 8: The first absorption of the complexes and their corresponding monomers

Parameters	ZINDO	TD/B3LYP/6 – 31G
Monomer A	473.09	370.27
Monomer B	503.41	419.75
Complex 1	529.52	660.77
Monomer A	469.99	491.49
Monomer B	503.41	419.75
Complex 2	1598.80	656.24
Monomer A	469.46	368.57
Monomer B	503.41	419.75
Complex 3	1602.16	751.57
Monomer A	470.32	492.18
Monomer B	503.41	419.75
Complex 4	1595.69	539.64
Monomer A	470.32	358.10
Monomer B	503.41	419.75
Complex 5	1574.69	562.40
Monomer A	469.73	358.83
Monomer B	503.41	419.75
Complex 6	1570.52	597.97
Monomer A	473.09	370.27
Monomer B	503.62	421.75
Complex 7	528.51	615.04

4.4 Infrared Spectrum

Vibrational spectroscopy is used to identify or analyze compounds. The vibrational spectrum of a molecule is considered to be a unique physical property and characteristic of the molecule. So, the following spectrum were observed using DFT/B3LYP method at 6-31G basis set

IR spectrum of monomer A of complex 1 had the following main vibrations. A band structure observed between 3051.4 and 3102.96 cm^{-1} was indicative of C = C – H of aromatic ring. A band at 1505.08 and 1407.16 cm^{-1} was due to C = C – C aromatic ring stretch. A band around 757.7 cm^{-1} was because of aromatic C – H out of plane bend. A band at 1293.75 cm-1 indicative of aromatic tertiary amine, C- N stretch and at 1242.22 cm^{-1} was aromatic primary amine, C- N stretch. A band at about 3339.74 and 3340.03cm^{-1} were indicatives of aromatic primary amine, N- H stretch. A band observed at 1644.26 cm^{-1} was due conjugated ketone.

IR spectrum of monomer B of complex 1 had the following main vibrations. The characteristic band of aldehyde was observed at about 2710.56 and 2712.96, and also at 1620 cm^{-1}. Aromatic ring stretch due to C = C – C was shown at 1493.87 cm^{-1}. A band observed at 1122.02 cm^{-1} was due to C – N stretch of tertiary amine. A band at 3368.09.and 3369.46 cm^{-1} was because of N – H stretch of primary amine, while at 1573.43 cm^{-1} was due to N – H bend of primary amine.

IR spectrum of complex 1 had the following main vibrations in addition of the vibrations of the monomers. A band structure observed at 3496.27 and 3498.43 cm^{-1} were indicative of aromatic amine, N – H stretch. The N – H stretch of the aromatic amine of the complex 1 was higher than the corresponding monomers due to increase in strength of N-H covalent bond in the complex [17].

Fig. 4: IR spectrum of monomer A

Fig. 5: IR spectrum of monomer B

Fig 6: IR spectrum of complex 1

5. Conclusion

Through DAD – ADA (D: donor, A: acceptor) triple hydrogen bonded complexes are likely to be formed. The triply hydrogen bonded complexes are stable. Steric effect due to the aromatic ring attached to monomer A hinders the formation of hydrogen bond in complexes 2 – 4. The bond length of single bond is shorter than the bond lengths of hydrogen bonds.

The absorption maximum of complexes was red – shifted comparing with their monomers, due to its less LUMO – HOMO energy gap. The energy gap of monomer A and complex 1 were 3.3485 and 1.5533 eV respectively.

The N – H stretch of the aromatic amine of the complex 1 was higher than the corresponding monomers. All characteristic vibration of monomer A and B are also shown on complex 1.

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