DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA'S COLLEGE (AUTONOMOUS)

ERNAKULAM

B.Sc. CHEMISTRY PROJECT REPORT

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Register Number : **AB21CHE007**
Year of Work : **2023-2024**

This is to certify that the project "**STUDY OF THE EFFECT OF SOLVENTS IN THE ELECTRONIC SPECTRA OF AROMATIC AZO COMPOUNDS BY EXPERIMENTAL AND DFT CALCULATIONS**" is the work done by **LUDUVEENA FRANCIS.**

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Submitted to the Examination of Bachelor's Degree in Chemistry

Date: 4/5/24

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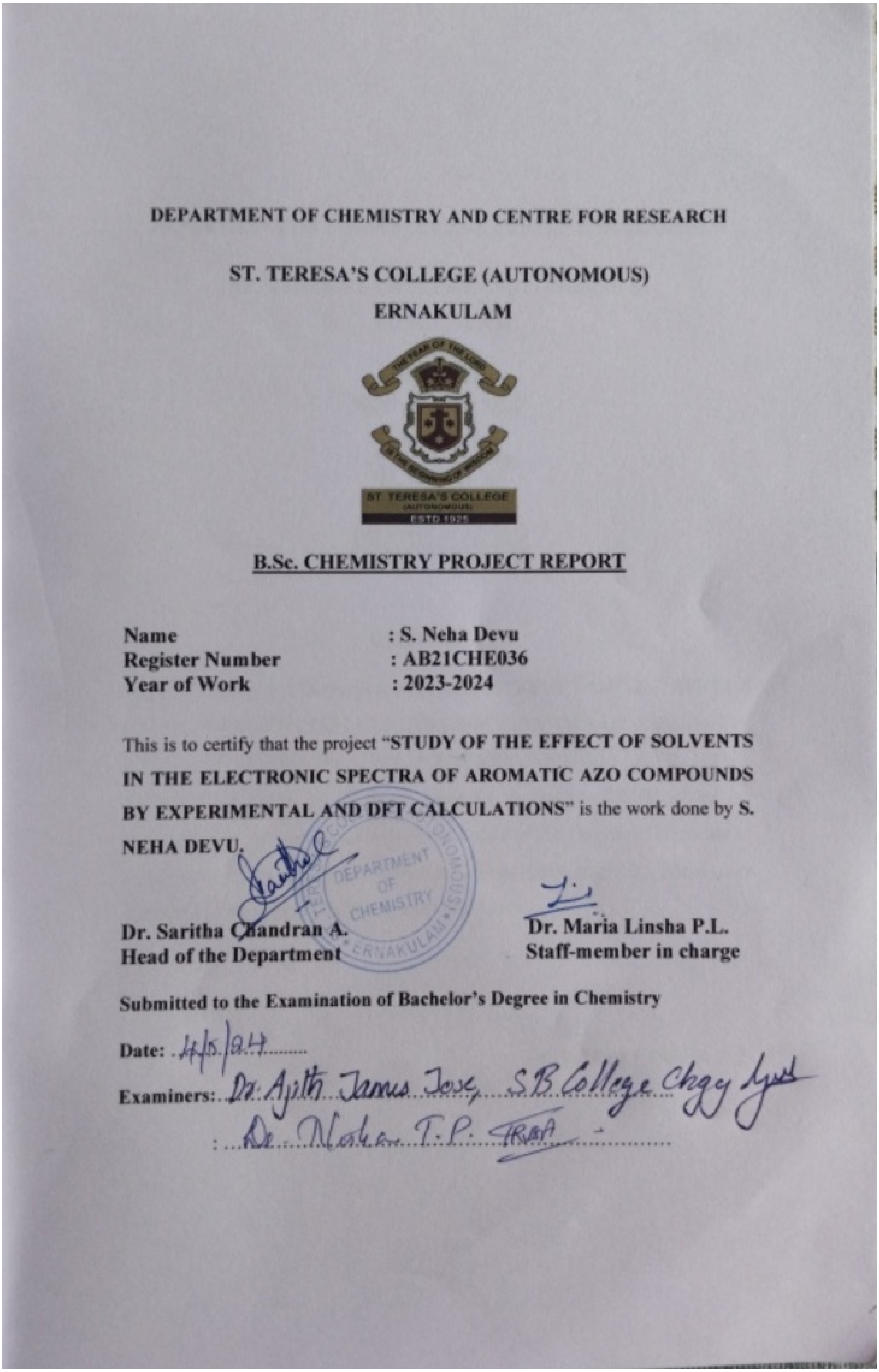

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

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Submitted to the Examination of Bachelor's Degree in Chemistry

Date: 14/5/24

Examiners: Dr. Ajith James Jose, S.B. College Chgy

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PROJECT REPORT

On

STUDY OF THE EFFECT OF SOLVENTS ON ELECTRONIC SPECTRA OF AROMATIC AZO COMPOUNDS BY EXPERIMENTAL AND DFT CALCULATIONS

Submitted by

LUDUVEENA FRANCIS (AB21CHE007)
RAMEESA LATHEEF (AB21CHE022)
ROSEBEN PAULSON (AB21CHE023)
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In partial fulfillment for the award of the

Bachelor's Degree in Chemistry

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA'S COLLEGE (AUTONOMOUS)
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2023-2024

DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

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Dr. Saritha Chandran A. **Dr. Ushamani M**
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Submitted to the Examination of Bachelor's Degree in Chemistry

Date: ……………........

Examiners: ………………………………………………………………..

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DEPARTMENT OF CHEMISTRY AND CENTRE FOR RESEARCH

ST. TERESA’S COLLEGE (AUTONOMOUS)
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CERTIFICATE

This is to certify that the project work entitled “**STUDY OF THE EFFECT OF SOLVENTS IN THE ELECTRONIC SPECTRA OF AROMATIC AZO COMPOUNDS BY EXPERIMENTAL AND DFT CALCULATIONS**” is the work done by **LUDUVEENA FRANCIS, RAMEESA LATHEEF, ROSEBEN PAULSON, S NEHA DEVU** under my guidance in the partial fulfilment of the award of the Degree of Bachelor of Science in Chemistry at St. Teresa’s College (Autonomous), Ernakulam affiliated to Mahatma Gandhi University, Kottayam.

Dr. MARIA LINSHA P L

Project Guide

DECLARATION

I hereby declare that the project work entitled "**STUDY OF THE EFFECT OF SOLVENTS IN THE ELECTRONIC SPECTRA OF AROMATIC AZO COMPOUNDS BY EXPERIMENTAL AND DFT CALCULATIONS**" submitted to Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of **Dr.MARIA LINSHA P L, Assistant Professor,** Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam and this project work is submitted in the partial fulfilment of the requirements for the award of the Degree of Bachelor of Science in Chemistry.

LUDUVEENA FRANCIS
RAMEESA LATHEEF
ROSEBEN PAULSON
S NEHA DEVU

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LUDUVEENA FRANCIS
RAMEESA LATHEEF
ROSEBEN PAULSON
S NEHA DEVU

Contents

Chapter 1

Introduction

1.1 Azo Compounds

Organic compounds with the functional group diazenyl (R−N=N−R′), where R and R′ can be either aryl or alkyl groups, are known as azo compounds. The IUPAC describes azo compounds as "Derivatives of diazene (diimide), HN=NH, wherein both hydrogens are substituted by hydrocarbyl groups, e.g. PhN=NPh azobenzene or diphenyl diazene.", where Ph stands for phenyl group. Two aryl groups are included in the more stable versions.

1.2 Aryl Azo Compounds

Typically, aryl azo compounds are crystalline, stable species. The prototypical aromatic azo compound is azobenzene. It is mostly found as the trans isomer, but when exposed to light, it changes to the cis isomer.

By means of an electrophilic substitution process known as azo coupling, an aryl ring—particularly one substituted with an electron-donating group—attacks an aryl diazonium cation to produce aromatic azo compounds.

$\mathrm{ArN{=}NAr'} + \mathrm{H}^{+} \rightarrow \mathrm{ArN}^{2+} + \mathrm{Ar'H}$

The azo coupling reactions are often carried out close to 0 °C since diazonium salts are frequently unstable close to room temperature.

Aryl azo compounds, particularly those with red, orange, and yellow hues, have vibrant colors as a result of π-delocalization. As a result, they are employed as dyes and are referred to as azo dyes; Disperse Orange 1 is one such example [1].

. Because the colors of some azo compounds acid and salt forms differ, they can be used as markers of acidity and base. One such example is methyl orange. Blue azo dye is used as the recording layer in the majority of DVD-R/+R and some CD-R discs. The broad development of azo compounds was spurred by the economic success of azo dyes.

The most significant artificial colorants, azo dyes are used extensively in the printing, paper, textile, and other industries.

The detrimental effects of azo dyes on aquatic life and people have prompted urgent requests for the treatment of effluents containing azo dyes in order to remove them or transform them into safe and beneficial goods.

Additionally, when the molecular weight of the azo dyes grew, the dispersion of colors in water also increased. This was most likely due to the azo dyes' increasing azo bond content, which slowed down the pace at which they degraded.

The majority of azo dyes are made by diazotizing an aromatic primary amine and then coupling it with one or more electron-rich nucleophiles, such hydroxy and amino acids [2].

Additional techniques for creating azo dyes include reducing nitroaromatic derivatives in an alkaline medium, reducing nitroso compounds by $AlLiH_4$, oxidizing primary amines with lead tetraacetate or permanganate potassium, condensing hydrazines and quinones, and condensing primary amines with nitroso derivatives.

The azo group may form bonds with enolizable aliphatic groups, aromatic heterocycles, benzene rings, and naphthalenes. These, in their many colors of varying strengths, are what give the dye its color.

An azo dye's backbone, auxochrome groups, chromophoric groups, and solubilizing groups generally indicate its chemical structure. The azo bonds and the chromophores and auxochromes they are connected to determine the colour of the azo dyes.[3]

1.3 Charge Transfer Compounds

Charge-transfer (CT) interactions—also known as donor-acceptor interactions—are often employed [4]. The binding constants of a CT pair are dependent on a variety of factors, including the substituents' steric effects, complementary charge distribution, and shape matching, in addition to the components' capacity to provide and receive electron density. For structurally simple D–A pairings, the association constants typically range from 100 to 102 M^{-1}, indicating that the solitary charge–transfer interaction is often fairly weak. However, much higher association constants are obtained when combined with other advantageous interactions, such as hydrogen-bonding or hydrophobic interactions. For this reason, CT complexes have been widely used to engineer the formation of supramolecular species with elaborate structures and functionalities. Molecular encapsulation is advantageous in increasing the value as well. The host can either directly participate in the CT interaction or create a segregated environment for the formation of a CT complex. Solvophobic interactions typically work in concert to favor the donor-acceptor interaction. Molecular encapsulation is another advantageous strategy for increasing the value of the association constant between a donor and an acceptor. Many complexes of the pseudorotaxane class take use of CT interactions [5].Because redox processes directly impact the electron density, electrochemistry is a particularly useful technique for managing the formation and dissolution of donor-acceptor complexes. As the solvent polarity is changed, charge transfer transitions frequently undergo a change in energy (a phenomenon known as solvatochromic change), which is caused by a change in the polarity of the complex involved. Charge-transfer bands and d-d transitions may be distinguished using this.

An electron from a photon's lower energy d orbital gets stimulated to a higher energy d orbital during the d-d transitions. Weak absorption results from d-d transitions. The charge transfer transitions are known as CT-transitions. Charge is transferred from a metal to a ligand or from a ligand to a metal during this transition.

When an electron moves from an atom or molecule to another similar entity, it is referred to as charge transfer. To do this, one item has to be free of electrons or have a propensity to shed electrons, and the other things need to be attracted to the electron.

Conduction, friction, and polarization are the three processes by which electrons can be transmitted. The overall charge stays the same in every instance. The law of conservation of charge is this. Direct contact between materials with different electron-accepting or electron-losing capacities results in conduction.

Research on how structure and optical behavior interact in various media might have fascinating real-world implications. The solute's chemical and physical characteristics are influenced by solvents. The kind and degree of solute-solvent interactions that form in the solute's solvation shell determine the solvent effect. Changes in electronic transitions are caused by the solvent, depending on how the solute interacts with it in both its excited and ground states. Utilizing the solvatochromic phenomenon, one may ascertain electro-optical properties including the solute's excited states and ground dipole moments. Dipole moment data may be used to clarify a molecule's geometrical and electrical structure, which is helpful for creating nonlinear materials. When the fluorescent light is stimulated, its dipole moment.

Emission tunability range as a function of medium polarity. Studies using solubility-chromic techniques on Schiff base compounds have demonstrated modifications to photophysical characteristics, including electronic configuration, ground and excited state dipole moments, and intra- and intermolecular interactions in solutions.

Since it can only rely on organic small molecules, the intramolecular charge transfer (ICT) feature has been widely explored among the range of photophysical processes that may influence the luminescence behaviors of a molecule [6]. Push-pull or donor-acceptor (D-A) units found in organic small molecules have drawn a lot of interest because they can support the ICT process, which further enhances their great optical qualities and positive structure-property connection. ICT-based organic small molecules have several intrinsic benefits, such as easy chemical tailoring, good reproducibility through synthesis and purification, and ease of incorporation into a wide range of device fabrications, including organic light-emitting diodes, dye-sensitized solar cells, colorimetric chemosensors, and non-linear optics. When photoexcited, ICT-based fluorophores with D-A systems enable modifications in the frontier molecular orbitals, resulting in a broad spectrum of emitters spanning from blue to red.

The literature has a wide range of electron push-pull dyes, most based on the chromophores rhodamine, quinoline, carbazole, dansyl, and borondipyrromethene (BODIPY). To achieve a simpler, more cost-effective method, however, the creation of donor-acceptor-containing compounds is still booming, particularly those with big Stokes shift and high fluorescence quantum yield. Because of their remarkable photoluminescence capabilities, coumarins have also been the subject of intense research among the vast array of electron push-pull dyes. For example, Deng et al. created a coumarin-dicyanoisophorone probe that provided a long emission wavelength in the near-infrared (NIR) region (λem = 710 nm) and a notably significant Stokes shift up to 222 nm for the detection of carbon monoxide. Li et al. synthesized vertically π-expanded coumarins with phenynyl and cyano groups, which showed a red-shifted emission up to 671 nm in DMF and an outstanding fluorescence quantum yield (ΦF = 0.80). Most coumarins have low energy emission, which makes them particularly useful for cell staining and bioimaging. Research teams from many universities have also lately looked into the use of coumarins in electrical applications.

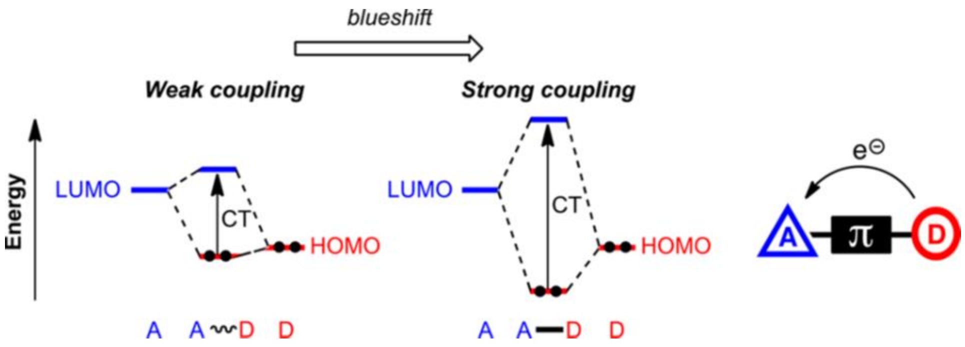
However, the structural framework of fluro[3,2-c]coumarin has received very little attention in terms of research on the molecular side and photoluminescence capabilities. A launching pad for achieving a π extended electron push-pull system through increased electron resonance and molecular planarity is provided by the furan ring fused inside fluro[3,2-c]coumarin. Extended π-conjugation may accelerate the excited state molecule's charge transfer process, resulting in longer wavelength emission, a higher Stokes shift value, and a smaller energy band gap.

The kind of substituents bonded to the primary chromophoric unit of a molecule is a crucial factor in adjusting its ICT character. Choosing the appropriate electron-donating (D) and electron-withdrawing (A) moiety will have an impact on the molecule's capacity for intramolecular charge transfer. The bathochromically shifted emission is caused by significant polarization in the excited state, which may be produced by altering the kind and location of substituents in the fluro[3,2-c]coumarin.[7]

An additional kind of contact is the one that takes place between molecules that are electron pair donors and donors (EPD-EPA or charge transfer interaction). Complexes having a mesomeric structure between two noninteracting molecules (D and A) and two components with ionic connections D+A–are produced as a result of this kind of interaction. Lewis bases, or electron donor molecules, and Lewis acids, or electron acceptor molecules, can be either n, σ, or π donors or acceptors, respectively. Their interaction energy ranges from 180 kJ/mol to as low as around 10 kJ/mol. when donor acceptor interactions occur. The only substances that have the propensity to form bonds primarily through electrostatic interactions are extremely strong Lewis acids and bases. The π orbitals are the molecular orbitals that are involved in the charge transfer for the majority of organic compounds having a π electronic system. The highest energy orbitals in the molecule are these π orbitals. Because of this, even though the π donor and π acceptor systems are weak Lewis acids and bases, they are commonly referenced amongst compounds.[8]

It is only reasonable to presume that the molecule has partial charges. For instance, OCH3 and Cl are electron donor groups, but NO2 is an electron withdrawing group. If an aromatic ring has one or more electron withdrawing groups, the π system will become a π-acceptor system and will be more likely to interact with a π-donor compound in a donor-acceptor type of relationship, even if they are weak Lewis bases and acids, respectively. For instance, weak charge transfer complexes containing olefinic double bonds are formed when silver cations particularly interact with unsaturated molecules. It is known that this kind of interaction may be used to improve separation in reversed-phase HPLC by separating cis-trans olefins by adding Ag+ to the mobile phase.

Charge transfer transition is an electronic transition in which the electron is transferred from the HOMO orbital which covers one part of the molecule, the donor region to the LUMO orbital which covers another part of the molecule, the acceptor region. The excitation energy of the charge transfer bands depends on the mode of coupling between the two regions. If the donor and acceptor regions are weakly coupled then lower will be the excitation energy. Compounds exhibiting this phenomenon of charge transfer transition will be intensely colored. This can be explained on the basis of the principle of Ultraviolet-visible spectroscopy.



Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb.[9]

1.4 Solvatochromism

Solvatochromism is the ability of a chemical substance to change color due to a change in solvent polarity. The Solvatochromic effect or Solvatochromic shift refers to a strong dependence of absorption and emission spectra with the solvent polarity . Influence of a solvent has a greater effect on the excitation energy and absorption wavelength of the molecule. The excitation energy depends on the solvent since the interaction of the solvent molecules with the substrate molecules affect the energy gap of the HOMO and LUMO orbitals. When a solvent of much higher polarity is used there is a stronger interaction present between the solute and solvent molecule. Such a case refers to the strongly coupled nature of the two orbitals with a reduced energy gap. Hence the wavelength of the light absorbed (λ_{max}) will be maximum.

There are mainly two types of Solvatochromism observed, Positive and Negative. Negative solvatochromism corresponds to hypsochromic shift with increasing solvent polarity. The corresponding bathochromic shift is termed as positive solvatochromism. The sign of solvatochromism depends on the difference in dipole moment between the ground and excited states of the chromophore.

Mohanadshakoor and co-workers have been studied the solvatochromic behaviors of two newly synthesized pyridocoumarins of different substituents. When the nitro-substituted pyridocoumarin was compared to the other H-pyridocoumarin, a new band developed in the visible range. This new band exhibited showed negative solvatochromic behavior, where $\lambda_{max,v}$ decreases with increasing solvent polarity.[10]

Solvatochromism is the reversible alteration of a material's absorption or emission spectrum brought about by the action of solvents. The absorption maximum shift, which results from variations in the solvation energy of the initial and excited states in different solvents, is what causes the color shift. In more polar solvents, the excited state, which is more polar than the starting state, is more stable. Such systems have a bathochromic shift in the absorption spectrum due to their decreased excitation energy requirements. Positive solvatochromism is the name given to these phenomena. The absorption maximum shifts hypsochromically and experiences a counter-effect due to the stimulated state being less polar than the original condition. We refer to this phenomenon as negative solvatochromism. Metal complexes make up the majority of solvatochromic materials. When solvent molecules interact with solute molecules, one or both of the orbitals participating in the electronic transition might become stabilized or destabilized, which affects the λmax and results in solute-solvatochromism. The Franck–Condon principle states that the speed of nuclei is substantially slower than the speed of electrons. Because the solvent molecules cannot reorient during electronic excitation, a solute-excited state experiences a ground-state solvent coordination sphere. This phenomenon manifests itself in $\pi \rightarrow \pi^*$ transitions, when the excited state frequently exhibits greater polarization than the ground state. In this case, the excited state will stabilize with the help of a polar solvent, resulting in a smaller energy gap. This causes λmax to move bathochromically to a longer wavelength.[11]

Azo compounds, known for their high photo-induced anisotropy, are excellent substrates for liquid crystals and efficient photorefractive media. Their photosensitivity and superior structuring properties are attributed to the lability of substituents binding to the N=N groups. Azo dyes typically show positive solvatochromism, but negative solvatochromism has been reported in neutral azo dyes with both electron-donating and -withdrawing moieties. More than 60% of all dyes are azo dyes, which are the most widely used type. Azo dyes make up about 70% of all dyes used in industry. The functional group (-N=N-) that unites two symmetrical, asymmetrical, identical, or non-azo alkyl or aryl radicals is what distinguishes these compounds.

These dyes are created using a straightforward diazotization process. The majority of azo dyes are made by diazotizing an aromatic primary amine and then coupling it with one or more electron-rich nucleophiles, like hydroxy and amino acids. Additional techniques for creating azo dyes include reducing nitroaromatic derivatives in an alkaline medium, reducing nitroso compounds using AlLiH4, oxidizing primary amines with lead tetraacetate or permanganate potassium, condensing hydrazines, and quinones. The N=N (azo) can be bonded to benzene rings, aliphatic or aromatic heterocycles.

By considering above views, the present project focused on the Solvatochromic effect of some selected azo compounds by experimental and DFT calculations.

Chapter 2

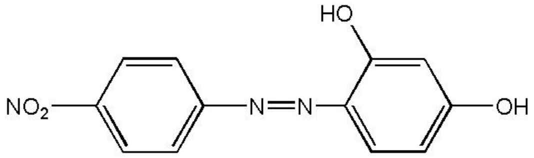
Materials and Methods

This chapter gives a brief description of the materials and experimental procedures adopted for the present investigation.

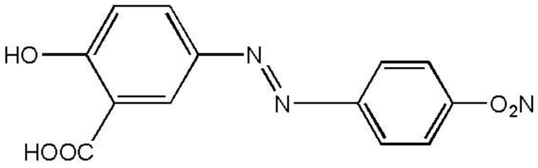
2.1. Experimental Section

The compounds synthesized for the present study are

1. 4-(Nitrophenyl)diazinyl benzene-1,3-diol (NAR)



2. 4-(Nitrophenyl)salicylic acid (NAP)



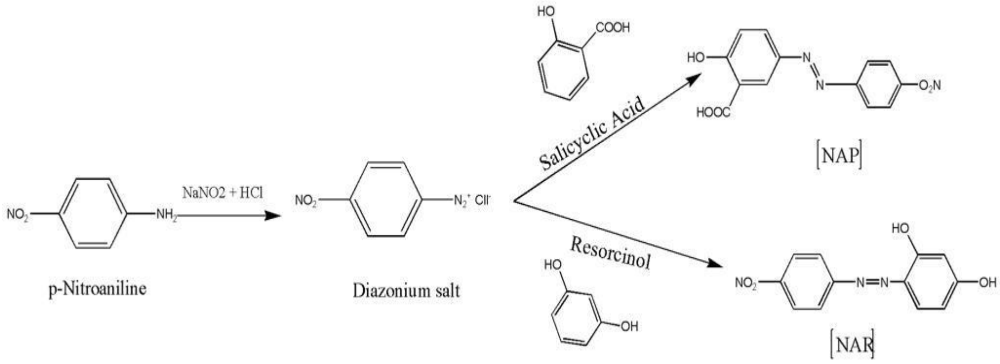
2.2. Chemicals Required

1. Conc. HCl
2. p-Nitroaniline
3. $NaNO_2$
4. Salicylic acid
5. Resorcinol
6. NaOH

7. NaCl

2.3 Synthesis of NAR and NAP

1.5 ml of water and 1.5 ml of HCl are taken and are mixed together in a test tube. This is kept in an ice water bath. 0.38 g of $NaNO_2$, 0.7 g of 4-Nitroaniline and 1.5 ml of water are taken and are mixed together in a 50 ml beaker. The contents of the beaker are rapidly stirred using a glass rod. The test tube is then removed from the ice water bath and the beaker is then kept in the ice water bath. The contents of the test tube are added to the beaker and is stirred gently for 10-15 minutes. A yellow precipitate is obtained which is then filtered using a glass funnel. Dissolve 0.74 g of salicylic acid (for NAP) or 0.56 g of resorcinol (for NAR) in 10 ml of 2.5 M aq. NaOH in another 50 ml beaker and is placed on a magnetic stirrer for 45 - 60 minutes. After the prescribed time the beaker is then placed in the ice water bath. Now the filtered yellow precipitate is slowly added into the beaker (in ice water bath) while stirring and stirring is continued for 10 minutes. The beaker is then removed from the ice water bath and then 1.5 ml of Conc. HCl and 1 g of NaCl are added to it and is then heated until dissolved. It is then cooled to room temperature and is again placed in ice water bath until the precipitation is complete. The solid obtained is finally filtered using vacuum filtration with a Buchner funnel and is washed with 5 ml of water approximately.



2.4 Methods

2.4.1 UV Visible Spectroscopy

The UV and visible spectra of compounds indicate electronic transitions between energy levels, typically between bonding or lone pair orbitals and non-bonding or antibonding orbitals, with the absorption intensity influencing the spectral wavelength.

Beer's law: It states that the faction of the incident light absorbed is proportional to the

number of the absorbing molecules in the light-path and will increase with increasing concentration or sample thickness.

Lambert's law: It states that the fraction of the monochromatic light absorbed by a homogenous medium is independent of the intensity of the incident light and each successive unit layer absorbs an equal fraction of light incident on it.

From these two laws, the following empirical expression, known as Beer-Lambert law, may be formulated.

$\text{Log} (I_0 /I) = \varepsilon cl= A$

Where,

I_0= intensity of incident light

I = intensity of emergent light

Ɛ =molar absorptivity

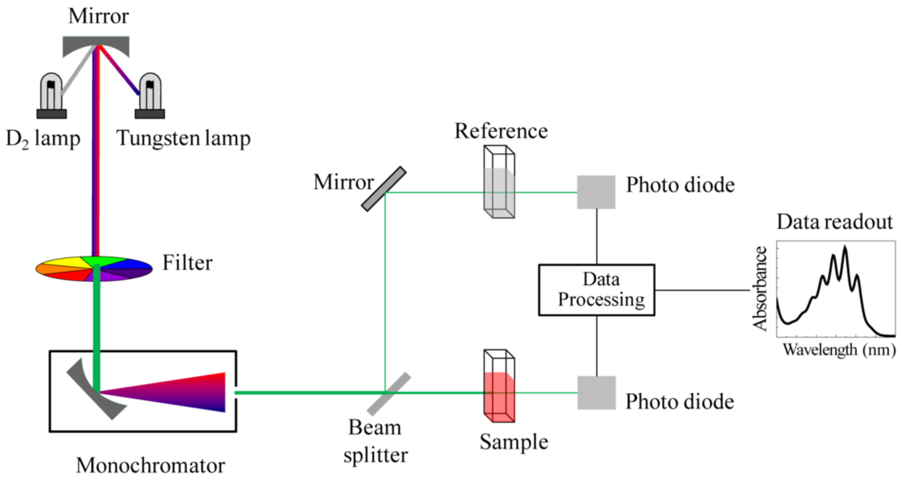
C = concentration of solute in moles/liter

L =path length

A =absorbance

UV Visible Instrumentation

A UV/Vis spectrophotometer is a tool used in ultraviolet-visible spectroscopy to measure the intensity of light passing through a sample and compare it to another light beam of the same intensity and wavelength. The transmittance ratio is calculated by comparing the intensity of the light beam with the light that did not pass through the sample. The spectrophotometer consists of a light source, sample holder, diffraction grating, prism, and detector. Radiation sources include Tungsten filament, Deuterium arc lamp, Xenon arc lamp, and LEDs. A detector is a device that collects light from various sources, such as photomultiplier tubes, photodiodes, arrays, or charge coupled devices (CCDs). Single photodiode detectors and tubes are used with scanning monochromators, which filter light to only reach the detector at one time. Fixed monochromators are used with CCDs and photodiode arrays, which can collect light of different wavelengths on different pixels or groups of pixels simultaneously.



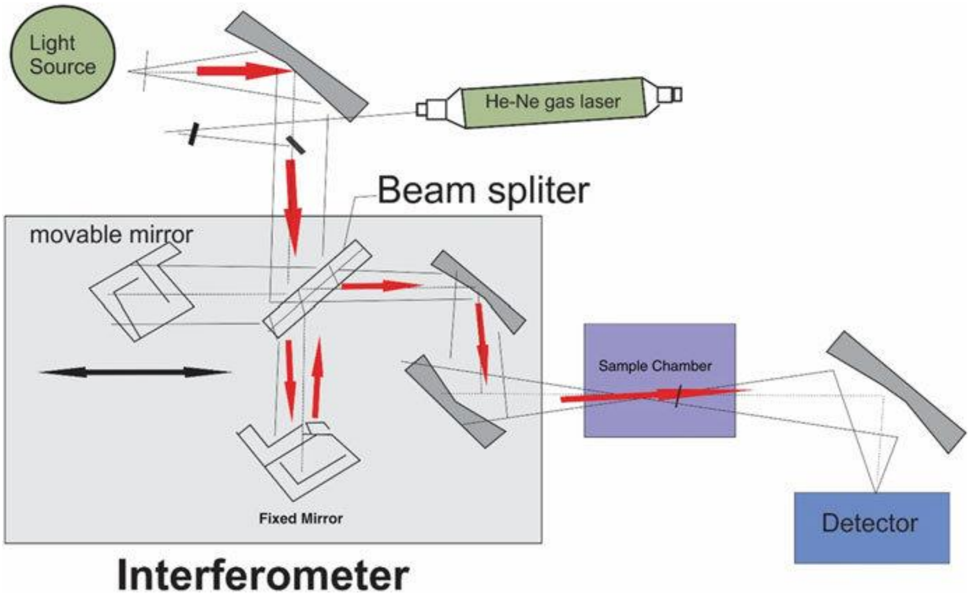
2.4.2. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a widely used technique to identify functional groups in materials like gas, liquid, and solid by measuring the absorption of infrared radiation by each bond in the molecule, resulting in a spectrum. Materials with covalent bonds absorb electromagnetic radiation in the IR region, which is lower energy and higher wavelength than UV-visible light and shorter than microwave radiation. To determine functional groups in a molecule, it must be IR active, with a dipole moment. When IR radiation interacts with the covalent bond of materials with electric dipoles, the bond starts back and forth oscillation, causing the change in the net dipole moment of the molecule. Atoms and symmetrical molecules cannot absorb IR radiation due to their lack of chemical bonds and zero dipole moment.[14]

Infrared radiation absorbs light, creating vibration modes, relating to molecule bond nature. FTIR spectrum measures wavenumbers (4000-600 cm−1), directly related to energy and frequency.

FTIR Instrumentation

The FTIR spectrometer is a system consisting of an IR light source, interferometer, sample compartment, detector, amplifier, and computer. The light source generates radiation that hits the sample, which is amplified and converted to digital signals. The interferogram is translated to spectrum using the fast Fourier transform algorithm. The main core of the spectrometer is the Michelson interferometer, which consists of a beam splitter, fixed mirror, and a moveable mirror. FTIR is a method for obtaining infrared spectra, involving collecting an interferogram of a sample signal, performing a Fourier transform, and displaying the spectrum.[15]



2.4.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance (NMR) is a physical phenomenon where nuclei in a strong constant magnetic field are disturbed by a weak oscillating magnetic field, producing an electromagnetic signal with a frequency characteristic of the nucleus. NMR is a powerful tool in modern science, capable of solving complex structures and interactions in heterogeneous samples, offering vast potential in environmental research.

The application of nuclear magnetic resonance (NMR) spectroscopy involves tuning a spectrometer to a specific nucleus, typically the proton. The simplest method is the continuous wave (CW) method, which involves spinning a sample in a glass tube, broadcasting radio frequency radiation, and monitoring the emission of absorbed radiation. The NMR spectrum is obtained by varying the magnetic field or adjusting the frequency of the radiation.[17]

2.4.4 Computational Chemistry

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. The main assumption is that the properties of molecules can be calculated by solving the Schrodinger equation for the molecule. While computational results normally complement the information obtained by chemical experiments, it can in some cases predict unobserved chemical phenomena. It is widely used in the design of new compounds.

The methods employed cover both static and dynamic situations. In all cases the computer time and other resources (such as memory and disk space) increase rapidly with the size of the system being studied. That system can be a single molecule, a group of molecules, or a solid. *Abinitio* (from first principle) methods are based entirely on quantum mechanics and basic physical constants. Other methods are called empirical or semi-empirical because they employ additional empirical parameters. Both ab initio and semi-empirical methods make the Born–Oppenheimer approximation, which greatly simplifies the underlying Schrödinger equation by assuming that the nuclei remain in place during the calculation compared to electrons. In principle, ab initio methods eventually converge to the exact solution of the underlying equations as the number of approximations is reduced. In some cases, the details of electronic structure are less important.[18]

Gaussian (software)

Gaussian is a computer program for computational chemistry initially released in 1970 by John Pople and his research group at Carnegie-Mellon University as Gaussian 70. It has been continuously updated since then. The name originates from Pople's use of Gaussian orbitals to speed up calculations compared to those using Slater-type orbitals, a choice made to improve performance on the limited computing capacities of then-current computer hardware for Hartree-Fock calculations. Originally available through the Quantum Chemistry Program Exchange, it has been developed and licensed by Gaussian, Inc. Gaussian quickly became a popular and widely used electronic structure program. Prof. Pople and his students and post-docs were among those who pushed the development of the package, to carry out cutting-edge research in quantum chemistry and other fields.[19]

Density functional theory (DFT)

DFT is a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure of molecules. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. It is based on two theorems proposed by Hohenberg and Kohn: [4] any ground state property of a molecule is functional of the electron density any trial electron density function will give energy higher than the true ground state energy. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. The accuracy of DFT methods using hybrid functionals is comparable to high level *ab initio* methods but it uses less computer time. One of the most popular hybrids functional is B3LYP which developed by Becke, Lee, Yang and Parr in 1993.[20]

Basic Set

Basis set is a set of mathematical functions, linear combinations of which yield molecular orbitals. The functions are usually centered on atomic nuclei. Standard basis sets for electronic structure calculations use linear combinations of Gaussian functions to form the orbitals. Gaussian offers a wide range of pre-defined basis sets, which may be classified by the number of types of basis functions that they contain. Basis sets assign a group of basis functions to each atom with in a molecule to approximate its orbitals. These basis functions themselves are composed of a liner combination of Gaussian functions; and the component Gaussian functions are referred to as primitives. A basis function consisting of a single Gaussian function is termed as uncontracted.

STO-3 G: This is called a minimal basis set. It has just enough contacted Gaussian functions for each atom.3 Gaussian primitives per function. A single Gaussian gives a poor representation of a slater function, but that this approximation can be improved by using a linear combination of Gaussians.

H;1s: C;1s,2s,2px,2py,2pz.

Double zeta basis set

Two sizes of contacted functions are used for each atomic orbital.

Split valence basis set

Multiple contracted Gaussians are used for valence atomic orbitals.

Eg: 3-21 G

The basis set split each valence orbital into two parts, an inner shell and an outer shell. The basis function of the inner shell is represented by two Gaussians, and that of the outer shell by one Gaussian; the core orbitals are each represented by one basis function, each composed of three Gaussians. Thus, H and He have a 1s orbital split into (1s inner) and (1s outer), for a total of two basic functions. 6-31G - 6 primitive Gaussians in one contracted core function. 2-contracted functions in valence region; one consisting of 3 gaussians and the other consisting of 1 primitive Gaussian.

Polarized basis functions

Molecules can be more accurately described by supplementing the split valence basis set with **d** functions, called polarization function. The term arises from the fact that d functions permit the electron distribution to be polarized. Polarization functions enable the SCF process to establish a more anisotropic electron distribution. The 3-21G basis set augmented where appropriate with **d** functions is called the 3-21G* or 3-21G(d) basis; the asterisk indicates polarization functions (d in this case), and the parentheses mean that the extra polarization functions are present only beyond the first row.

B3LYP

Hybrid functionals are a class of approximations to the exchange correlation energy functional in density functional theory (DFT) that incorporate a portion of exact exchange from Hatreefock theory with exchange and correlation from other sources (ab initio, such as LDA, or empirical). The exact exchange energy functional is expressed in terms of the Kohn Sham orbitals rather than the density, so is termed an implicit density functional. One of the most commonly used versions in B3LYP, which stands for Becke, 3-parameter, Lee-Yang-Parr.

Chapter 3

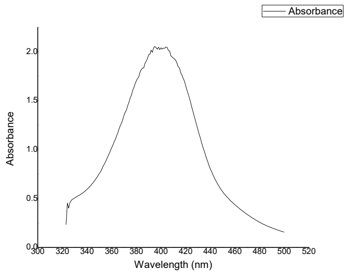
Results and discussion

Two azo compounds, NAR and NAP are synthesized by coupling reaction between p-Nitroaniline and Resorcinol (NAR) and p-Nitroaniline and Salicylic acid (NAP). The precipitate formed is filtered, dried and recrystallized. The compounds were characterized by UV-Visible, Infrared and Nuclear Magnetic Resonance Spectroscopic methods. Solvatochromic effect of the compounds were studied by experimental and DFT calculations, since HOMO and LUMO orbitals of the compounds are located at two different ends of the same molecule.

3.1 Characterization of Compounds NAR and NAP

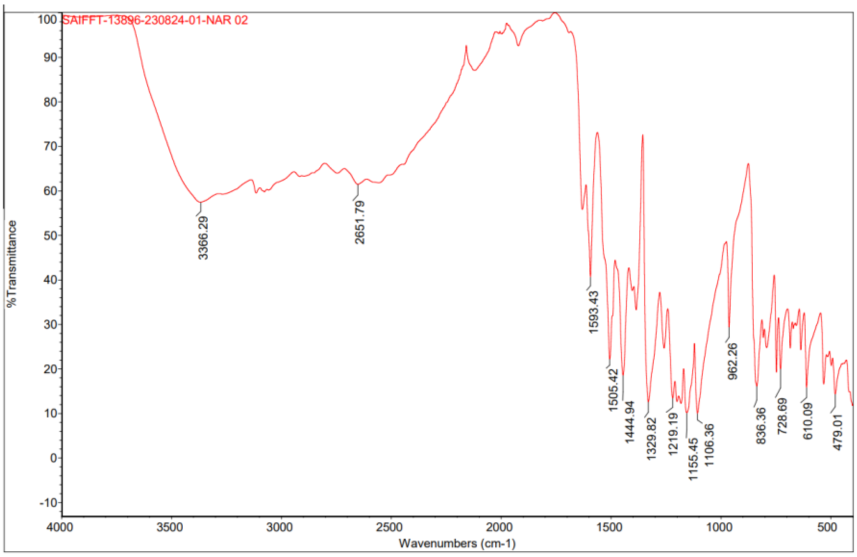
Compound 1 – NAR

3.1.1 UV-Visible Spectroscopy



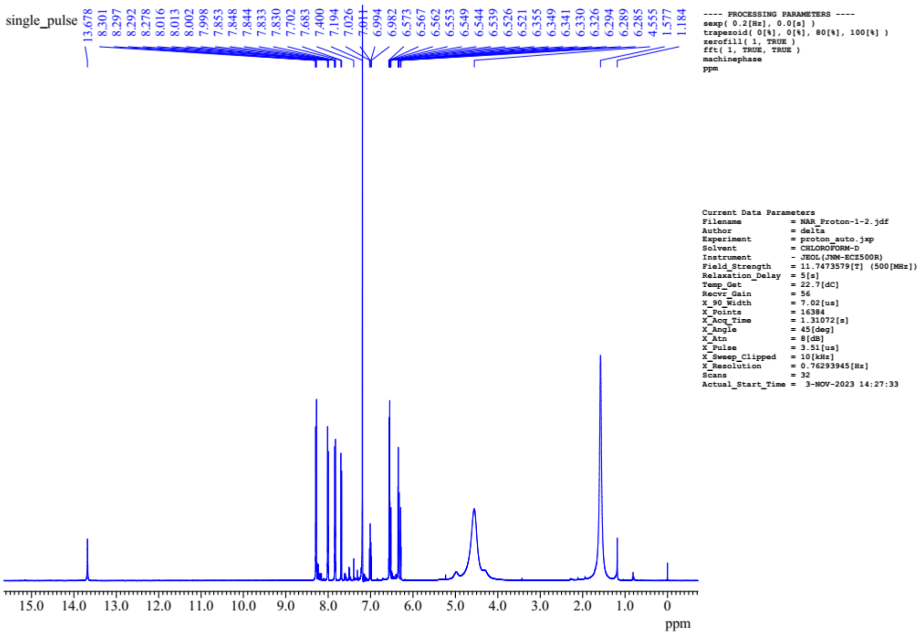
Solvent	λ_{max}Measured
Acetone	399

3.1.2 FTIR Analysis



From the literature reference the IR characteristic frequency of NO_2 group is between 1600-1500 cm^{-1} and 1400-1300 cm^{-1}. The above graph of the analysis of the compound also shows a peak in the range between that of NO_2 group. This confirms the presence of NO_2 group in the compound. The frequency of OH group from reference is found to be between 3300-2500 cm^{-1}. From analysis the compound NAR has also got a peak in this range. This confirms the presence of OH group in the compound.

3.1.2 NMR Analysis



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fft( 1, TRUE, TRUE )
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ppm
```

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Author             = delta
Experiment         = proton_auto.jxp
Solvent            = CHLOROFORM-D
Instrument         - JEOL(JNM-ECZ500R)
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Relaxation_Delay   = 5[s]
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Recvr_Gain         = 56
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X_Points           = 16384
X_Acq_Time         = 1.31072[s]
X_Angle            = 45[deg]
X_Atn              = 8[dB]
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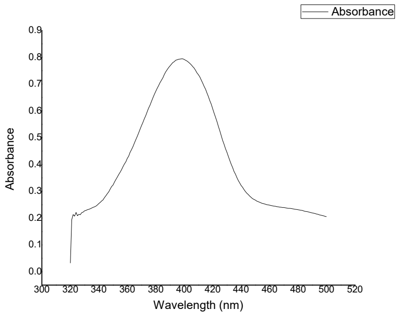
The chemical shift values between 7-9nm corresponds different benzene ring protons regards to different substitution and between 4-5ppm corresponds to two -OH groups

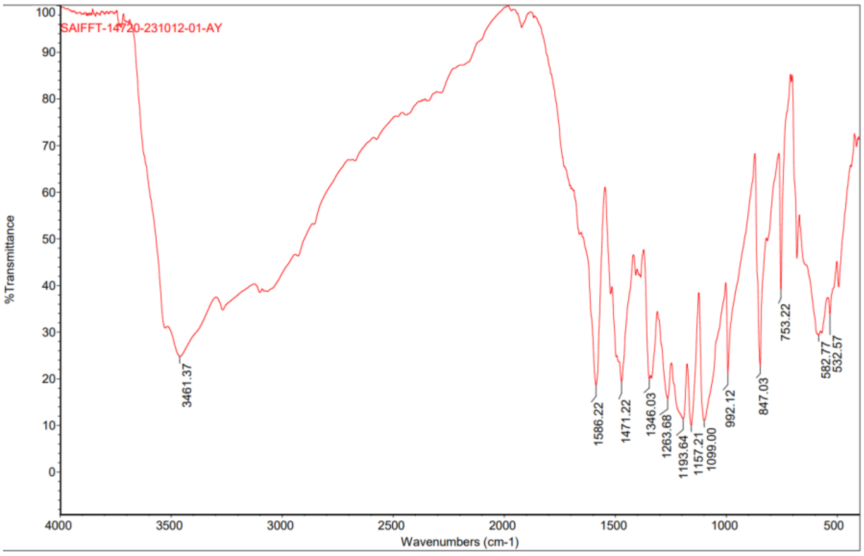
<u>Compound 2- NAP</u>

3.1.4 UV Visible Analysis



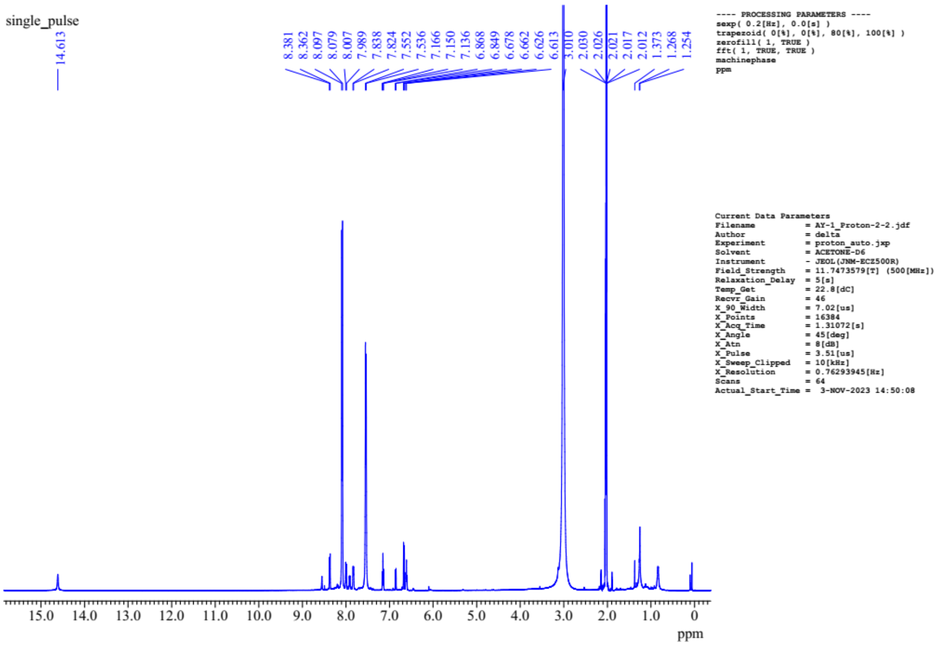
Solvent	λ_{max} Measured
Acetone	398.5

3.1.5 FTIR Analysis



From the literature reference the IR characteristic frequency of NO_2 group is between 1600-1500 cm^{-1} and 1400-1300 cm^{-1}. The above graph of the analysis of the compound also shows a peak in the range between that of NO_2 group. This confirms the presence of NO_2 group in the compound. The frequency of OH group from reference is found to be between 3300-2500 cm^{-1}. From analysis the compound NAR has also got a peak in this range. This confirms the presence of OH group in the compound. The frequency of COOH group from reference is found to be with the OH stretch between 3300-2500 cm^{-1} and C=O between 1760-1690cm^{-1}.

3.1.6 NMR Analysis



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fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
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Author             = delta
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Solvent            = ACETONE-D6
Instrument         - JEOL(JNM-ECZ500R)
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Relaxation_Delay   = 5[s]
Temp_Get           = 22.8[dC]
Recvr_Gain         = 46
X_90_Width         = 7.02[us]
X_Points           = 16384
X_Acq_Time         = 1.31072[s]
X_Angle            = 45[deg]
X_Atn              = 8[dB]
X_Pulse            = 3.51[us]
X_Sweep_Clipped    = 10[kHz]
X_Resolution       = 0.76293945[Hz]
Scans              = 64
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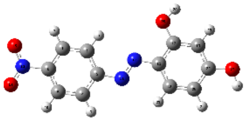
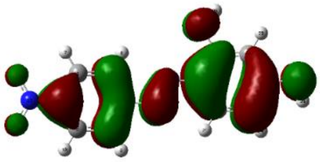
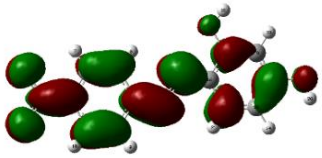
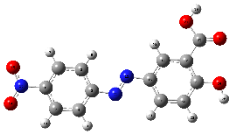
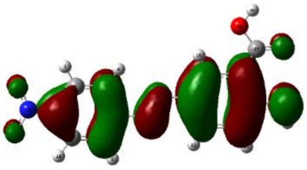
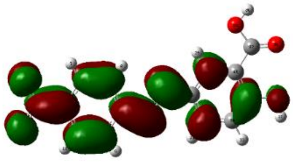
The Chemical shift value 14.6ppm corresponds to -COOH functional group,peaks between 7-9nm corresponds different benzene ring protons, and at 4ppm corresponds to -OH group

3.2 Solvent Effect on UV-Visible Absorption Spectra – Solvatochromism

3.2.1 DFT Calculations

The geometry optimization of the compounds NAR and NAP were performed by DFT calculations. The ground state optimized structure and HOMO and LUMO orbitals of the selected NAR and NAP, in the absence of solvent are given in **Table 1**.The HOMO and LUMO orbitals cover different regions of the molecules. Re-optimization of the compounds in various solvents show similar arrangement for the two orbitals and show that the electronic transitions occur from the HOMO to the LUMO orbital. Hence the absorption band in the UV spectrum corresponds to a CT transition.

Table 1 DFT Optimized structure, HOMO and LUMO orbitals of compounds 1 and 2 without solvent

Compound	HOMO	LUMO
 **NAR**	 -0.21608	 -0.09617
 **NAP**	 -0.23969	 -0.11196

The HOMO and LUMO orbitals of NAR and NAP in different solvents with increasing solvent polarity such as Acetone, Dichloromethane and Chloroform, are given in Table 2.and Table 3 respectively.

Table 2 HOMO and LUMO orbitals of compound NAR

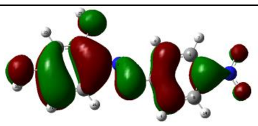
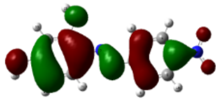
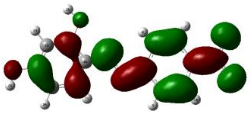
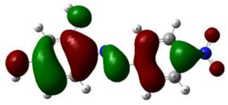
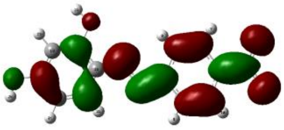
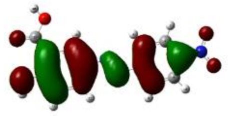
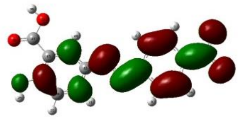
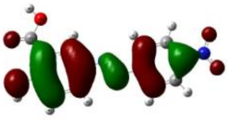
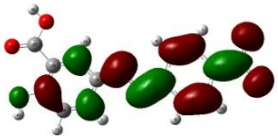
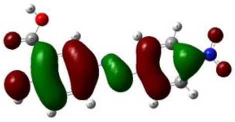
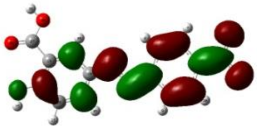
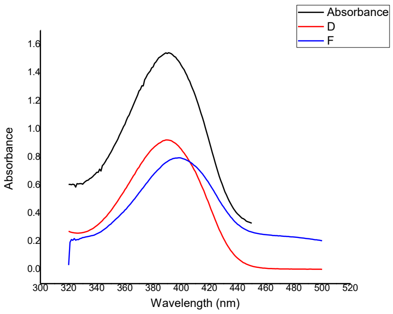
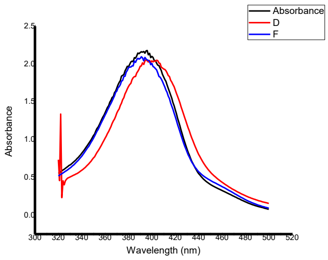
Solvent	HOMO	LUMO	HOMO-LUMO gap in eV
Acetone			3.06
Dichloromethane			3.10
Chloroform			3.13

Table 3 HOMO and LUMO orbitals of compound NAP

Solvent	HOMO	LUMO	HOMO-LUMO gap in eV
Acetone			3.31
Dichloromethane			3.32
Chloroform			3.49

The HOMO LUMO gap is calculated by subtractiong HOMO orbital energy from the energy of LUMO orbital and it is decreases with increase in solvent polarity. The absorption maxima values are calculated for NAR and NAP in different solvents and it is increases with increase in solvent polarity.

To compare the calculated absorption maxima values with the measured value, UV-Visible spectra of two azo compounds were measured in same solvents of different polarities. Both compounds show shortest wavelength for absorption maximum in non-polar solvent chloroform and largest absorption maximum is observed in polar solvent Acetone. With increasing solvent polarity, the absorption maxima of these compounds show a positive solvatochromic effect, Table 4.

<table>
<tr><td colspan="2">Table 4 The UV Visible absorption spectra of NAR and NAP in Acetone, Dichloromethane and Chloroform</td></tr>
<tr><td>NAR</td><td>NAP</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

The positive solvatochromic shifts are observed in both calculation and measurement, Table 5.

Table 5 Calculated and measured absorption maxima value of NAR&NAP in different solvents

Solvent	**NAR (1)**			**NAP(2)**		
	λ_{max}	Calc. λ_{max}	HLG eV	λ_{max}	Calc. λ_{max}	HLG eV
Chloroform	391	395.2	3.13	389.	369	3.4
Dichloro methane	396	399.9	3.10	391	372.7	3.32
Acetone	399	404.7	3.06	398.5	374.4	3.31

The calculated and measured absorption maxima values of NAR NAP increases with increase in solvent polarity.

Chapter 4

Conclusions

Two azo compounds of p-nitroaniline with Resorcinol and Salicylic acid were synthesized and characterized by UV, IR and NMR Spectroscopy. The geometry optimization of the compounds were done DFT calculations using Gaussian software. The calculation results show that the HOMO and LUMO orbitals of the compounds are not covering similar regions of the same molecule and the transition occurs from HOMO to LUMO orbital and hence the absorption band in the UV spectrum corresponds to a charge transfer transition. The presence of changes in solvent, affects the CT process and has a great influence on the energy gap between the orbtals.

The UV-Visible absorption spectra of azo compounds were recorded experimentally and by DFT calculations in different solvents having different polarities such as chloroform, dichloromethane and acetone, out of which Acetone>Dichloromethane>Chloroform is the order of increasing solvent polarity. The position and intensities of absorption bands are modified with changes in solvent polarity. Both calculated and experimentally measured λ_{max} values are increases with increase in solvent polarity i.e. exhibits positive solvatochromism**.**

References

[1] S. Benkhaya, S. M’rabet, and A. El Harfi, “Classifications, properties, recent synthesis and applications of azo dyes,” *Heliyon*, vol. 6, no. 1, p. e03271, Jan. 2020, doi: 10.1016/j.heliyon.2020.e03271.

[2] N. N. Mohd Yusof Chan, A. Idris, Z. H. Zainal Abidin, H. A. Tajuddin, and Z. Abdullah, “Intramolecular charge transfer-induced solvatochromism and large Stokes shifts of furocoumarins,” *Mater Chem Phys*, vol. 276, p. 125406, Jan. 2022, doi: 10.1016/j.matchemphys.2021.125406.

[3] C. Reichardt, “Solvatochromic Dyes as Solvent Polarity Indicators,” *Chem Rev*, vol. 94, no. 8, pp. 2319–2358, Dec. 1994, doi: 10.1021/cr00032a005.

[4] M. Shkoor, H. Mehanna, A. Shabana, T. Farhat, and A. D. Bani-Yaseen, “Experimental and DFT/TD-DFT computational investigations of the solvent effect on the spectral properties of nitro substituted pyridino[3,4-c]coumarins,” *J Mol Liq*, vol. 313, p. 113509, Sep. 2020, doi: 10.1016/j.molliq.2020.113509.

[5] T. Rijavec and S. Bračko, “Smart dyes for medical and other textiles,” in *Smart Textiles for Medicine and Healthcare*, Elsevier, 2007, pp. 123–149. doi: 10.1533/9781845692933.1.123.

[6] Diya Patel and Diya Panchal, “A Review on UV Visible Spectroscopy,” *A Review on UV Visible Spectroscopy*, vol. 10, no. 10, Oct. 2022.

[7] S. A. Khan, S. B. Khan, L. U. Khan, A. Farooq, K. Akhtar, and A. M. Asiri, “Fourier Transform Infrared Spectroscopy: Fundamentals and Application in Functional Groups and Nanomaterials Characterization,” in *Handbook of Materials Characterization*, Cham: Springer International Publishing, 2018, pp. 317–344. doi: 10.1007/978-3-319-92955-2_9.

[8] A. J. Simpson, M. J. Simpson, and R. Soong, “Nuclear Magnetic Resonance Spectroscopy and Its Key Role in Environmental Research,” *Environ Sci Technol*, vol. 46, no. 21, pp. 11488–11496, Nov. 2012, doi: 10.1021/es302154w.

[9] C. Reichardt, “Solvatochromic Dyes as Solvent Polarity Indicators,” *Chem Rev*, vol. 94, no. 8, pp. 2319–2358, Dec. 1994, doi: 10.1021/cr00032a005.

[10] M. Shkoor, H. Mehanna, A. Shabana, T. Farhat, and A. D. Bani-Yaseen, “Experimental and DFT/TD-DFT computational investigations of the solvent effect on the spectral properties of nitro substituted pyridino[3,4-c]coumarins,” *J Mol Liq*, vol. 313, p. 113509, Sep. 2020, doi: 10.1016/j.molliq.2020.113509.

[11] T. Rijavec and S. Bračko, “Smart dyes for medical and other textiles,” in *Smart Textiles for Medicine and Healthcare*, Elsevier, 2007, pp. 123–149. doi: 10.1533/9781845692933.1.123.

[12] Dr. Justin Tom, “UV-Vis Spectroscopy: Principle, Strengths and Limitations and Applications,” Jun. 2021.

[13] D. P. K. P. Prof. M. D. Dr. U. U. Diya Patel1, “A Review on UV Visible Spectroscopy,” Oct. 2022.

[14] A. Fadlelmoula, D. Pinho, V. H. Carvalho, S. O. Catarino, and G. Minas, “Fourier Transform Infrared (FTIR) Spectroscopy to Analyse Human Blood over the Last 20 Years: A Review towards Lab-on-a-Chip Devices,” *Micromachines (Basel)*, vol. 13, no. 2, p. 187, Jan. 2022, doi: 10.3390/mi13020187.

[15] Dr. Simon Thain, “IR Spectroscopy and FTIR Spectroscopy: How an FTIR Spectrometer Works and FTIR Analysis,” Sep. 2022.

[16] “Nuclear magnetic resonance (NMR) imaging for evaluation of reinforced concrete structures B. Wolter, Non-Destructive Evaluation of Reinforced Concrete Structures: Non-Destructive Testing Methods,” 2010.

[17] T. S. 2 S. A. I. F. M. S. Z. and Z. K. Komal Zia, “Nuclear Magnetic Resonance Spectroscopy for Medical and Dental Applications: A Comprehensive Review”.

[18] N. O. H. A. V. Garrett B. Goh, “Deep learning for computational chemistry,” Mar. 2017.

[19] “Errol Lewars: Computational chemistry: Introduction to the theory and applications of molecular and quantum mechanics,” 2011.

[20] “arr R G and Yang W, Density-functional theory of atoms and molecules,” 1989.