

Synthesis and Spectral Characteristics of Substituted 2,6-Dibenzylidene Cyclohexanone

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of
Science in Chemistry



Khulna University of Engineering & Technology

Khulna-9203, Bangladesh

May, 2018

Dedicated

To

my beloved

Parents

Declaration

This is to certify that the thesis work entitled "Synthesis and Spectral Characteristics of Substituted 2,6-Dibenzylidene Cyclohexanone" has been carried out by Hasan Md. Ashekul Islam in the department of Chemistry, Khulna University of Engineering and Technology, Khulna-9203, Bangladesh. The above work has not been submitted anywhere for the award of any degree or diploma.

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This is to certify that the thesis work entitled "Synthesis and Spectral Characteristics of Substituted 2,6-Dibenzylidene Cyclohexanone" has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of M.Sc in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh in May, 2018.

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Abstract

The design and synthesis of substituted 2,6-Dibenzylidene cyclohexanone based bis-chalcone derivatives were studied in this research through one of the most important Claisen-Schmidt condensation reaction of donor-acceptor conjugated system and their spectral properties has been studied. A number of substituted 2,6-Dibenzylidene cyclohexanone was synthesized through the reaction of commercially available para substituted benzaldehyde and cyclohexanone in presence of basic NaOH, where NaOH acts as a catalyst. The structures of the synthesized products were characterized by their physical, chemical and UV, IR & ^1H NMR spectra. The compounds were soluble in most organic solvents. 2,6-Bis-(4-dimethyl-amino benzylidene)-cyclohexanone showed acidochromic behavior with the change of pH. This compound when interacts with acids changed the color of compounds due to the presence of chromophore. 2,6-Dibenzylidene-cyclohexanone **1** absorbed at 330 nm and 2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone **5** disclosed high absorption at 452 nm. The bathochromic shifts for compound **5** is due to the presence of electron donating $\text{N}(\text{CH}_3)_2$ substituents and the hypsochromic shifts for compound **1** is mainly due to the basic chalcone framework where no substituent is present. Also 2,6-Bis-(4-methoxy-benzylidene)-cyclohexanone **4** showed absorption at 359 nm (bathochromic shifts, lesser than compound **5**) due to the presence of electron donating MeO substituents. Probably the halogen substituent contributed very little effect to the absorption and hence 2,6-Bis-(4-chloro-benzylidene)-cyclohexanone **2** exhibited absorption at 333 nm. Further 2,6-Bis-(4-nitro-benzylidene)-cyclohexanone **3** showed absorption at 340 nm.

The solvatochromic behavior study of these compounds revealed that when these compounds were dissolved in different solvents (Ethanol, Ethyl acetate and Dichloromethane) formed hydrogen bonds on the basis of the polarity of the solvent and stabilized the product. EtOH is a polar protic solvent and the polarity of ethanol is more than ethyl acetate and dichloromethane hence in case of compounds 1, 4 & 5 exposed greater λ_{max} (bathochromic shifts) in EtOH due to the formation of hydrogen bonds. This shifts turned to hypsochromic from ethyl acetate to DCM as these are aprotic. This could be due to the decrease in energy of the excited state as a function of increase in solvent polarity, which is in the order: $\text{DCM} < \text{Ethyl acetate} < \text{EtOH}$ and stabilized the compound.

Chapter 1

Introduction

Chapter 1

Introduction

Chalcones are α , β -unsaturated ketone containing the reactive keto ethylenic group and are categorized as bichromophoric molecules that possess keto-vinyl moiety $-\text{CO}-\text{CH}=\text{CH}-$ which act as precursor for biologically important heterocyclic compounds. Chalcones and bis-chalcones are prominent secondary metabolites and predecessors of flavonoids and isoflavonoids in plants [1]. Chalcones are natural compounds that are largely distributed in plants, fruits, and vegetables [2].

Chalcone forms the central core for a variety of important biological compounds, which are known collectively as chalcones or chalconoids. Chalcones can be prepared by an aldol condensation reaction between benzaldehyde and acetophenone in the presence of sodium hydroxide as a catalyst.

Dibenzylidene-cyclohexanone is a cyclohexanone based bis-chalcone [3]. It is an interesting compound which shows the characteristic property of chalcone due to the intramolecular torsional motions and cis-trans isomerization in the α , β -unsaturated ketone [4].

Cyclohexanone based bis-chalcone is a generic term given to compounds bearing the 2,6-dibenzylidene cyclohexanone framework, which can be functionalized in the propane chain by the presence of olefinic, keto or hydroxyl groups [5-6].

Benzylideneacetophenone is the parent member of the chalcone series. Chemically, chalcones have a structure formed of two aromatic rings with a various array of functional groups linked by α , β -unsaturated carbonyl groups. On both of the benzene rings, chalcones possess a system of conjugated double bonds and completely delocalized electrons [7-8]. Chalcone bears a very good synthon so that variety of novel heterocycles with good pharmaceutical profiles can be designed [9]. These are coloured compounds because of the presence of the chromophore $-\text{CO}-\text{CH}=\text{CH}-$, which depends in the presence of other auxochromes [10].

Though a variety of methods are available for the synthesis of chalcones, the most convenient method is the one that involves the solvent-free Claisen-Schmidt condensation of equimolar quantities of a substituted benzaldehyde with cyclohexanone in the presence of alkali (NaOH) for the synthesis of donor-acceptor (D-A) conjugated cyclohexanone

based bis-chalcones. Claisen-Schmidt condensation reaction occurs through the formation of nucleophile [11]. The nucleophile attacks the carbonyl carbon. When molecules with alpha hydrogens to a carbonyl group are treated with a base like sodium hydroxide (NaOH) enolate ions are formed. The enolate ion then reacts with cyclohexanone to give the product.

Subsequent dehydration of the β -hydroxycarbonyl compounds affords α -alkylidene or α -arylidene compounds [12-13]. Although studies on the Claisen-Schmidt reaction have been focused on α -alkylidene and α -arylidene-carbonyl compounds, interest in α, α' -bis alkylidene and α, α' -bis arylidene-carbonyl compounds is increasing [13]. Particularly, α, α' -bis-(substituted benzylidene)-cycloalkanones have been attracting much more attention, not only due to their stimulating biological activities such as antiangiogenic, quinine reductase inducer, arginine methyltransferase inhibitor, cytotoxicity, cholesterol-lowering activity, uses in agrochemicals, pharmaceuticals and perfumes, in bis-spiropyrrolidines, and as liquid crystalline polymer units, but also as important precursors for the synthesis of pyrimidine derivatives and they are the synthetic intermediates of choice to functionalize the α, β -position during the total synthesis of natural products such as the cystodytins [14-16].

The functional properties of the donor-acceptor compounds are highly dependent on the nature of the aromatic conjugation that unites the donor and acceptor fragments [17]. The donor-acceptor interaction in such molecules is mainly dependent on the nature of the conjugating unit [18].

Recently, chalcones have fascinated the interest of investigators because of their considerable purposes in multiple fields [19]. A photochromic compound is characterized by its ability to alternate between two different chemical forms having different absorption spectra in response to irradiation of appropriate wavelengths [20-21].

Cyclohexanone based bis-chalcones plays a vital role in many biological processes as well as an important intermediate for medicinal applications and is an area of continued attention for chemists and biologists [22-23]. The presence of α, β -unsaturated carbonyl system of chalcone makes it biologically active [24]. These molecules exhibit a wide range of pharmacological properties, like antibacterial, antifungal, antimalarial, anticancer, antiviral, anti-inflammatory, anti HIV, antitumor, antioxidant, immunosuppressive, antiprotozoal, antihyperglycemic and antituberculosis activities [25-27]. In fact, the pharmacological properties of chalcones are due to the presence of both α, β -unsaturation

[28]. Licochalcone A, an oxygenated chalcone, first isolated from roots of Chinese licorice, showed antimalarial activity in both in vitro and in vivo systems [29]. It is also used as chemotherapeutic agents [30]. Also some derivatives of this class of compounds are known as inhibitors of ovarian cancer cell proliferation and pulmonary carcinogens [31-32].

Moreover, chalcones are widespread as natural products in the plant kingdom and plays an essential role in a flower's pollination [33]. Therefore, chalcones are the subject of continuous experimental and theoretical investigations. Chalcones and cyclohexanone based bis-chalcones have a great importance in medicinal chemistry [34-35].

An interesting feature of chalcone is that they serve as starting materials for the synthesis of various heterocyclic compounds such as pyrimidines, pyrazolines, flavones, flavonols, flavanones, aurones and benzoyl coumarones as well as certain compounds like deoxybenzoins and hydantions which are of some therapeutic importance [36-38].

Chalcones are used to synthesize several derivatives like cyanopyridines, pyrazolines, isoxazoles and pyrimidines having different heterocyclic ring systems [39]. A number of compounds that have been researched for developing pharmaceutically important anti microbial agents, flavonoidal derivatives chalcones, flavanones and flavones have played an important role [40].

Flavonoids have attracted wide attention due to their important physiological activities and distinct functions [41]. Flavonoids form a large group of naturally occurring organic compounds and possess wide range of pharmacological actions including potential antimicrobial actions [42]. Moreover, flavonoidal derivatives acquire a special place in natural chemistry and in heterocyclic chemistry because this system is a frequently encountered structural design in many pharmacologically relevant compounds [43].

Compounds containing electron donor-acceptor moieties exhibit an intra-molecular charge transfer (ICT) excited state. The emission from such an ICT state exhibits marked solvatochromic behavior [44]. This is due to the sudden creation of a giant dipole which results in a strong interaction with the surrounding medium, causing not only solvent reorganization but also, sometimes, and structural rearrangement in the solute itself.

In recent years, chalcones have been used in the field of material science and for the development of pH sensors [45]. Although the determination of pH with traditional electrochemical sensor is well established, optical sensors can still be valuable alternatives. The photophysical properties of several chalcones containing electron donor substituents have been studied [46]. These compounds have been extensively used for various optical

applications including photo-alignment layer of liquid crystal displays, photo refractive polymers and fluorescent probes for sensing DNA or metal ions [47]. The photophysical and optical properties of several derivatives of chalcones with different substituent have been studied [48]. Chromophores changes the color of compounds on interaction with acids, termed as acidochromism, which is very important in the sensor industry.

Fluorescence resonance energy transfer (FRET) is an excited-state energy transfer process from the initially excited donor chromophore to an acceptor moiety via long range dipole–dipole interactions. The efficiency of FRET strongly depends on the degree of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, the distance between the donor and the acceptor, and their orientation [49].

In recent years, there have been many fluorescence probes based on FRET where most of them are confined to systems containing two organic fluorophores of high fluorescence quantum yields. Organic materials featuring donor- π -bridge-acceptor have continued to attract wide attention owing to their potential applications as red emitting charge transporters in organic light emitting devices (OLED), as semiconductors in thin film transistors (TFT), and as sensitizers in excitonic solar cells (DSSC) electro-optical properties. These dipolar compounds are also attractive due to their application in the sensor industry. In a suitably designed donor-acceptor compound, modulation of the donor or acceptor property by the interaction of analyte leads to the signal amplification. These dipolar compounds are typically constructed using an aromatic π -linker which facilitates the interaction between the donor and acceptor moieties. Frequently, triarylamine or heterocyclic bases such as carbazole, phenothiazine, etc. are used as donor fragments, while depending on the targeted applications electron-accepting moieties such as dicyanovinyl, cyanoacrylic acid, oxadiazole, benzothiadiazole, pyrazine/quinoxaline, and their aromatic fused analogs served as an acceptor group [50].

The development of new strategies for the preparation of organic molecules in neat condition is a challenging area of organic synthesis. A large number of methods are available for the synthesis of organic compounds which are carried out under anhydrous condition using volatile organic solvents like benzene, which are the cause of environmental problems and are also potentially carcinogenic. Hence, it is required to develop safe, practical and environment friendly process. This can be accomplished by just grinding the solids together using mortar and pestle, a technique known as Grindstone Chemistry. The reactions are initiated by grinding, with the transfer of very small amount

of energy called exothermic reaction. So in this research our interest is to synthesis the compound through solvent-free reaction.

Here we have focused on the synthesis of α, α' -bis-(substituted-dibenzylidene cyclohexanone) derivatives by solvent free Claisen-Schmidit reaction and their spectral characteristic properties have been studied [51]. Various substituted dibenzylidene cyclohexanone was prepared from cyclohexanone and different substituted benzaldehyde. These compounds were characterized by UV-Visible, IR and ^1H NMR spectroscopy. Photo physical properties were studied with different solvents to elucidate the interaction parameters

Chapter 2

Literature Review

Chapter 2

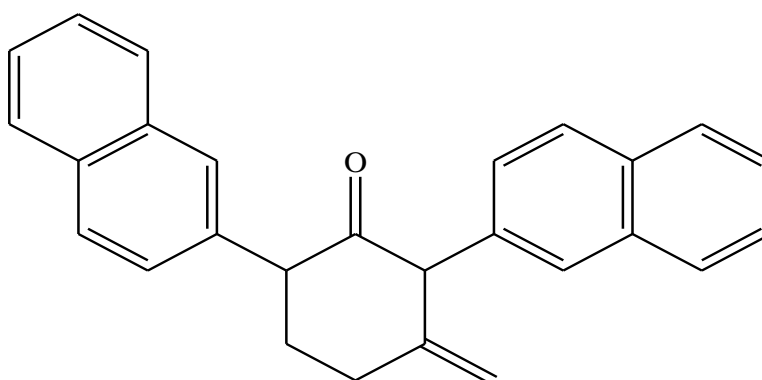
Literature Review

The findings from literature that, Chalcones and bis-chalcones are the major classes of naturally occurring organic compounds that are frequently found in plants, fruits and vegetables. Chalcones and their derivatives have medicinal, pharmacological as well as other various applications.

Dibenzylidene-cyclohexanone is a cyclohexanone based bis-chalcone which shows the characteristic property of chalcone.

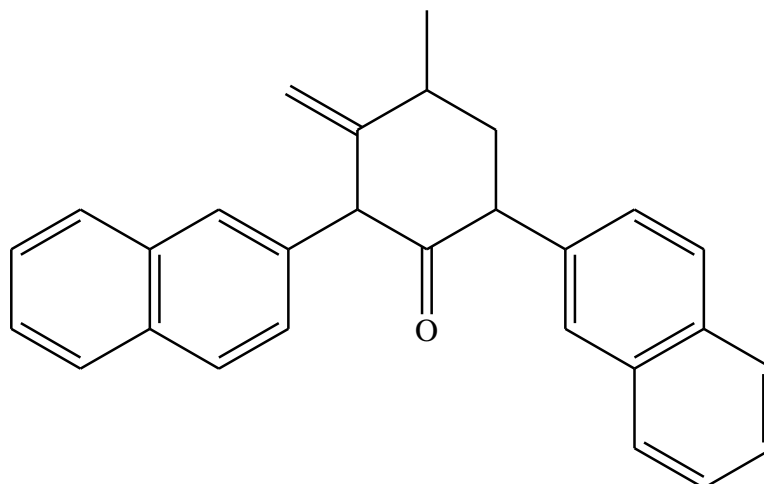
Cyclohexanone based bis-chalcone is a generic term given to compounds bearing the 2,6-dibenzylidene cyclohexanone frame work.

Motiur et al., 2012, prepared 2,6-Bis naphthalen-2-ylmethylene-cyclohexanone and 4-Methyl-2,6-bis naphthalene-2-ylmethylene-cyclohexanone from cyclohexanone and substituted benzaldehyde through Solvent-free Claisen-Schmidt reactions and they found quantitative yields (96-98%) [52].



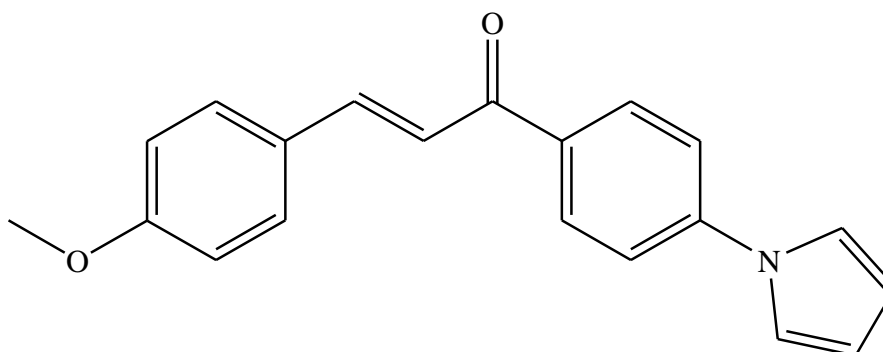
2,6-Bis naphthalen-2-ylmethylene-cyclohexanone

Additionally, they examined the regioselectivity of the Claisen-Schmidt reaction of acetone with benzaldehyde.



4-Methyl-2,6-bis naphthalene-2-ylmethylene-cyclohexanone

Satish K. A. et al., 2009, synthesized 3-(4- methoxyphenyl)-1-(4-pyrrol-1-yl-phenyl) prop-2-en-1-one and studied their antimalarial activity [53].

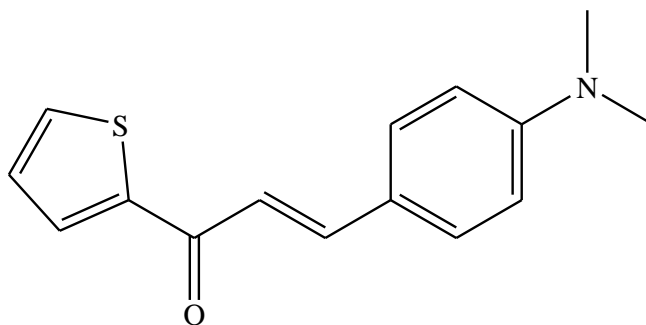


3-(4- methoxyphenyl)-1-(4-pyrrol-1-yl-phenyl) prop-2-en-1-ones

They suggested that chalcones are a class of compounds that provides an option of developing inexpensive, synthetic therapeutic antimalarial agents in the future.

Gaber M. et al., 2007, Studied the absorption and fluorescence characteristics of 3-(4-dimethylaminophenyl)-1-(2-thienyl) prop-2-en-1-one (DMATP) in different solvents [54].

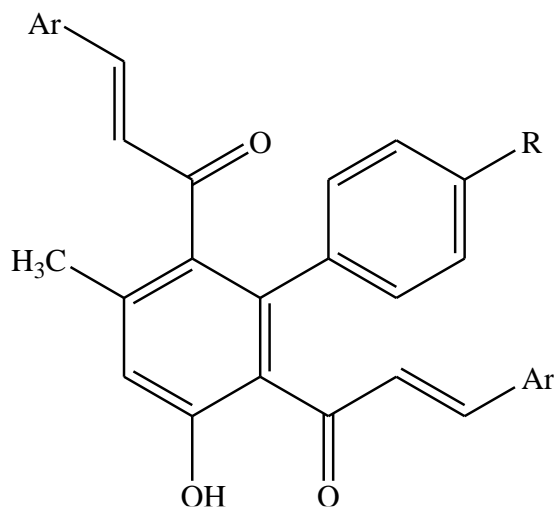
They also showed that DMATP dye exhibits a large red shift in both absorption and emission spectra as solvent polarity increases, indicating a large change in the dipole moment of molecules upon excitation due to an intramolecular charge transfer interaction.



3-(4-dimethylaminophenyl)-1-(2-thienyl) prop-2-en-1-one

The fluorescence quantum yield depends strongly on the properties of the solvents, which was attributed to positive and negative solvatokinetic effects. The excitation energy transfer from 7-dimethylamino-4-methyl coumarine (DMC) to DMATP has been also studied in CHCl_3 and the values of energy transfer rate constant and critical transfer distance. The photoreactivity and net photochemical quantum yield of DMATP in chloromethane solvents are also determined.

Anindra Sharma et al., 2010, synthesized A series of (2E, 2'E)-1,2-(3-hydroxy-5-methylbiphenyl-2,6-diyl)-bis(3-phenylprop-2-ene)-1-ones by the reaction of 1,3-diacetyl biphenyls with different aldehydes in presence of catalytic amount of solid KOH in ethanol in excellent yields [55].



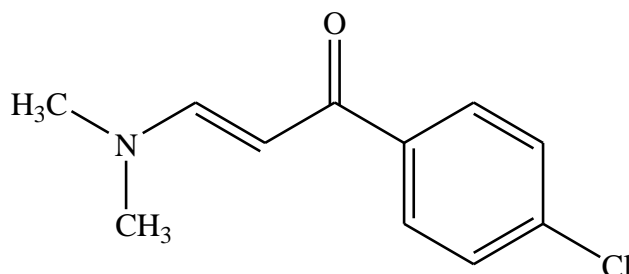
(2E, 2'E)-1, 2-(3-hydroxy-5-methylbiphenyl-2,6-diyl)-bis(3-phenylprop-2-ene)-1-one

The compounds were evaluated for anticancer activity against human breast cancer MCF-7 (estrogen responsive proliferative breast cancer model) and MDA-MB-231 (estrogen independent aggressive breast cancer model) cell lines, HeL a (cervical cancer) cell line,

and human embryonic kidney (HEK-293) cells. Most of the compounds preferentially inhibited the growth of the aggressive human breast cancer cell.

Ali M.K.M. et al., 2017, prepared thin films of a chalcone, 1-(4-chlorophenyl)-3-(4-N, N dimethyl amino phenyl)-2-propen-1-one (CDP) [56].

They reported that chalcone was dissolved in acetone with different concentrations to achieve thin films of different thicknesses. The solution was deposited by spin coating technique on glass substrates. The optical spectra of the chalcone thin films (CDP-TFs) were recorded.

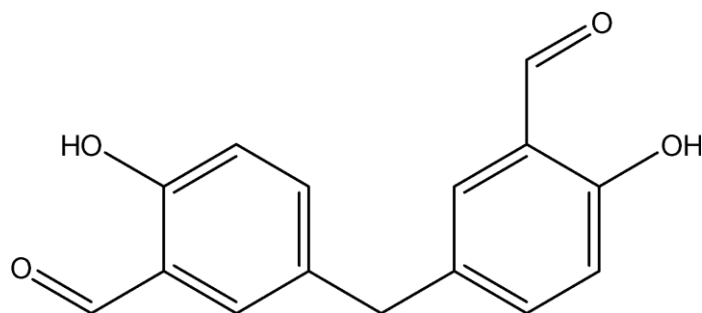


1-(4-chlorophenyl)-3-(4-N, N dimethyl amino phenyl)-2-propen-1-one

They characterized the product through FTIR, DRS, ^1H NMR, TGA and DSC and the chalcone properties were investigated as powder and thin films.

The findings revealed that the variations of the thickness from 150 to 400 nm had led increasing the crystal size from 2.92 to 78.51 nm. In contrast, the macrostrain was shifted to lower values. Furthermore, the energy band gaps of CDP-TFs increased by increasing the film thickness. That was a unique report on the structural and optical properties of chalcone as thin films.

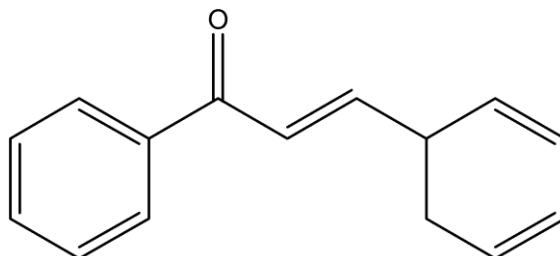
Nagaraj A. et al., 2008, prepared a series of novel bis-chalcones by the reaction of 5,5'-methylene-bis-salicyl aldehyde with various acetophenones, subsequent treatment with thiourea or guanidine resulted to the corresponding bis-thiazines or bispyrimidines in good yields [57].



5,5'-methylene-bis-salicyl aldehyde

They characterized all the compounds by IR, ^1H NMR, MS and elemental analysis. The antibacterial, antifungal and anti-inflammatory activities of the compounds had also been evaluated.

S. Sridhar et al., 2011, prepared A series of new chalcones bearing the 1,3-diphenyl-prop-2-en-1-one frame work by Claisen-Schmidt condensation of 3-acetyl-2,5-dimethylfuran with various substituted aromatic aldehydes in presence of aqueous solution of potassium hydroxide and ethanol at room temperature [58].

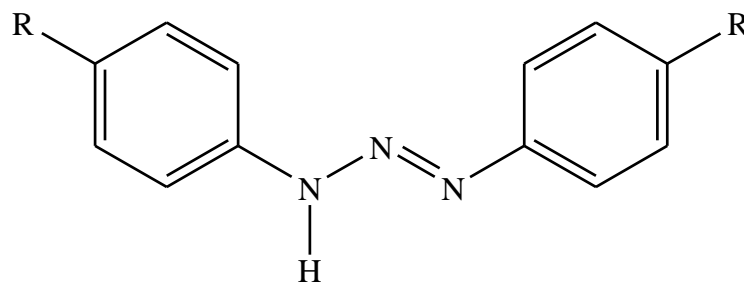


1,3-diphenylprop-2-en-1-one

They characterized the synthesized chalcones by means of their IR, ^1H NMR spectral data and elemental analyses. These chalcones were evaluated for antimicrobial and anti-inflammatory activities, some of them were found to possess significant activity, when compared to standard drugs.

Masoud et al., 2013, synthesized a series of diazoaminobenzene derivatives in which the substituents had a wide range of electronic characters are set out to understand the involvement of the substituent identity in controlling the changes in their electronic

absorption spectra [59]. They observed that the interactions between the diazoamino group and the different groups account for some spectral shifts.



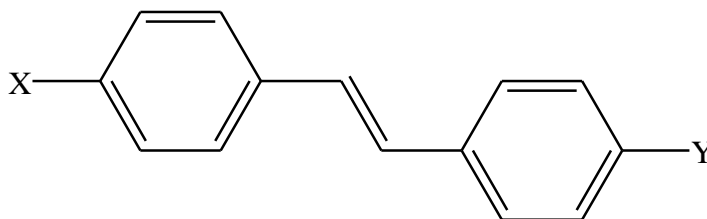
Diazoaminobenzene

They also measured the UV–Vis spectrum of each compound in several solvents with wide variations of solvent polarity parameters to examine the role of the chemistry of the solvent in these spectroscopical changes. The electronic transitions were assigned and the solvent induced spectral shifts which were analyzed in relation to the different solute–solvent interaction mechanisms using computational chemistry.

The regression analysis was applied for correlating the different parameters. The results helped to assign the solute–solvent interactions and the solvatochromic potential of the investigated compounds.

They concluded that the electronic character of the substituent and the chemical nature of the solvent was the major factors for the observed solvatochromism.

CAO Chen Zhong. et al., 2011, synthesized twenty five samples of 4,4'-disubstituted stilbene derivatives and determined their UV absorption max wavelengths in over 10 kinds of solvents including cyclohexane, ether, chloroform, acetonitrile and ethanol, in which 242 experimental data were recorded. They also discussed the effects of substituents and solvents on the energy of their UV absorption max wavelengths. The research results showed: the energy of UV absorption max wavelengths of 4,4'-disubstituted stilbenes was mainly affected by their intramolecular structure (substituent effect) in a given solvent, that is, the energy was dominated by both of excited-state substituent parameter and polar substituent constant [60].



4,4'-disubstituted stilbene derivatives

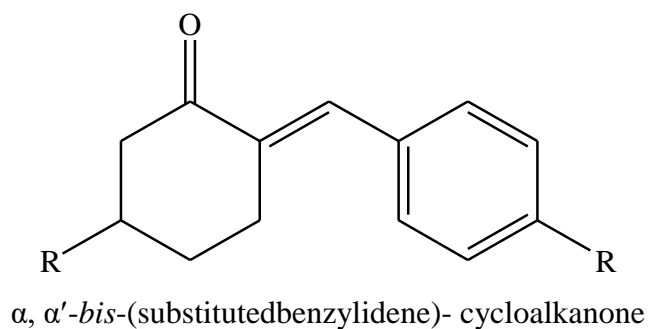
This means that their energy was dominated by the substituent effect and solvent effect in different kinds of solvents. An equation quantifying the energy of UV absorption max wavelengths of 4,4'-disubstituted stilbenes was developed.

In addition, they found that the *n*-octanol/water partition coefficient ($\log P$) is more effective than the solvatochromic dye (*ET*(30)) in scaling the solvent effect. The equation employed the parameter $\log P$ had a better correlation and more specific physical meaning. Further, the energies of UV absorption max wavelengths of some reported compounds were predicted by the obtained equation, which were in agreement with their experimental values.

Filip Bures, 2014, studied the Property tuning in selected examples of D- π -A molecules and summarized in this review article. The tuning and structure-property relationships had demonstrated on the particular A, π and D parts of the push-pull molecule. Special emphasis had been put on the tuning of the FMO levels and optical properties. Further prospective applications of the given chromophore had also been considered in his article [61].

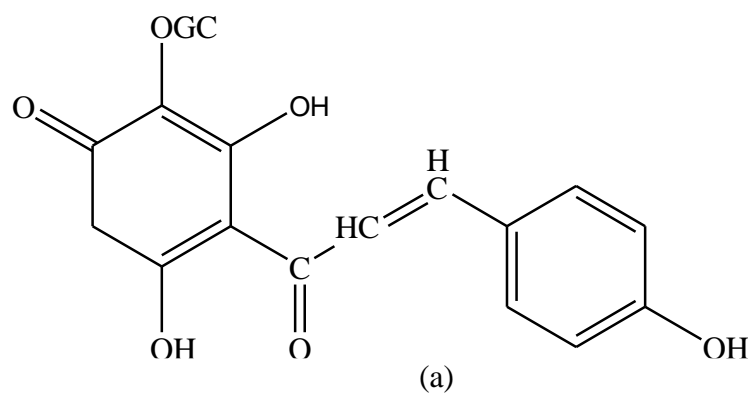
Adnan A. et al. 2012 synthesized α, α' -bis-(substitute-dbenzylidene)-Cycloalkanones from reactions of cycloalkanones with various substituted benzaldehydes (aryl aldehydes) using solid NaOH through Solvent-free Claisen-Schmidt condensation reaction [62].

They showed that aliphatic aldehydes also provided α, α' -bis-(substituted-alkylidene)cycloalkanones in very good yields with minor amounts of α -(substituted-alkylidene) cycloalkanones.

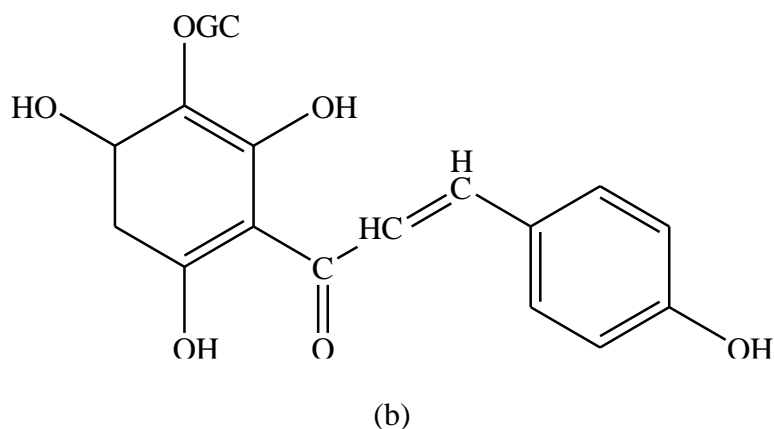


They also examined the catalytic performance of solid NaOH and the molar ratio of NaOH and the catalytic effect of solid NaOH was also evaluated by comparing it with KOH, NaOAc, and NH₄OAc and it turned out that 20% of solid NaOH was good enough to catalyze the Claisen-Schmidt reactions of cycloalkanones with various substituted benzaldehydes. Additionally they examined the regioselectivity of the Claisen-Schmidt reaction of acetone with benzaldehyde.

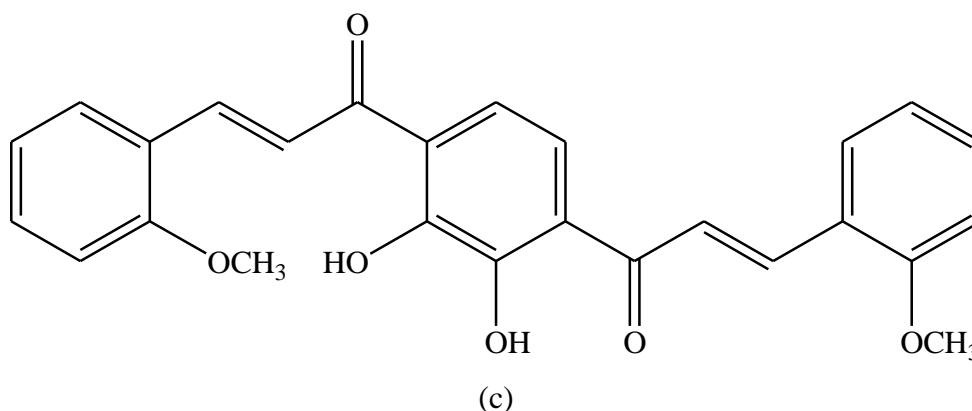
Perkin et al., 1987, first isolated Carthamin (a), a red pigment with green iridescence using pyridine solvent from the flowers of *carthamus tinctoria* (safflower) by and this was the first known example of chalcone in nature [63].



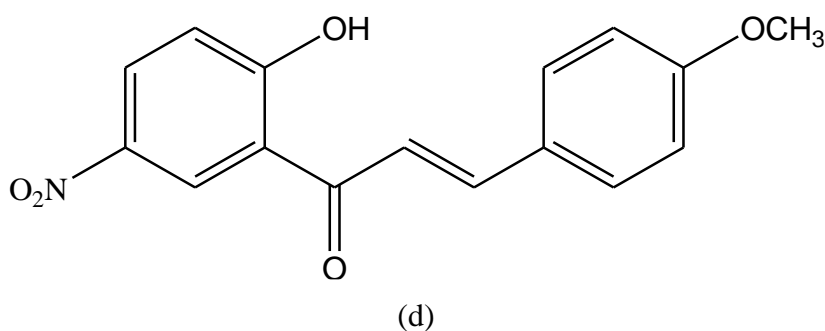
It isomerizes to a yellow compound isocarthamin (b) on treatment with dil. HCl as reported by Kuroda et.al., 1990 [64].



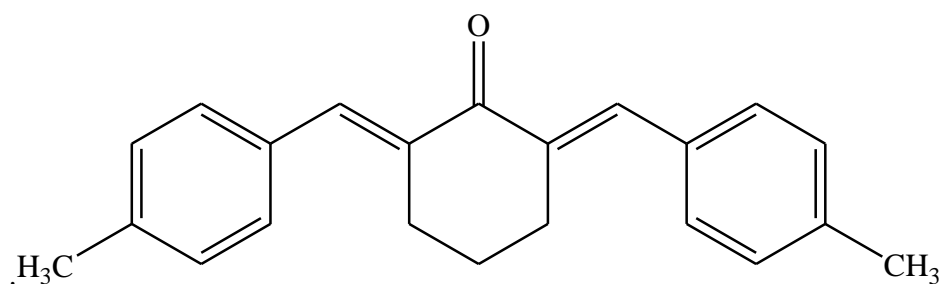
Venkatraman et al., 1993, prepared bis-chalcone (c) from dihydroxy-diacetyl benzene and anisaldehydes using alkali [65].



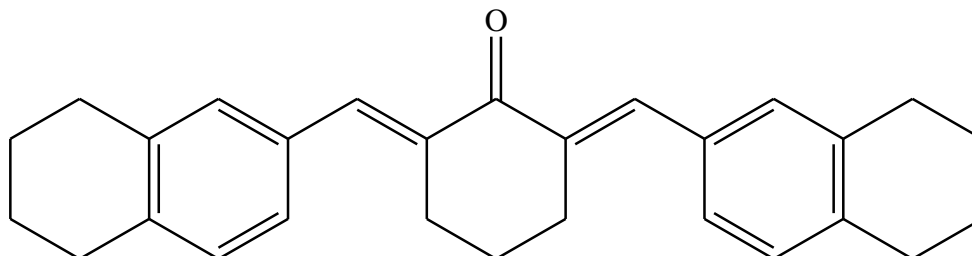
Sasaki et al., 1994, synthesized several hydroxy-nitrochalcone (d) using dry hydrogen chloride gas. They used hydrochloric acid to form 2-hydroxy-5-nitroacetophenone and p-anisaldehyde [66].



Usama et. Al., 2012, synthesized a series of novel N-substituted arylidene, pyrazole, thioxopyrimidine and thiazolopyrimidine derivatives by initial reactions of 2-methylcyclohexanone with aromatic aldehydes to give 2,6-dibenzylidene-3-methylcyclohexanone [67].



Some of the synthesized compounds were tested as antimicrobial agents. The detailed synthesis, spectroscopic data, and antimicrobial activities of the synthesized compounds were reported [68].



2-(1,2,3,4-Tetrahydronaphthalene-6-yl)-methylene)-6-(1,2,3,4-tetrahydronaphthalene-7-yl)-
methylene-cyclohexanone

CHAPTER 3

Experimental

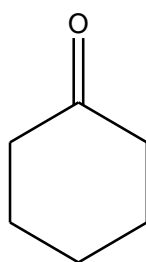
CHAPTER 3

Experimental

3.1 Reagent

Cyclohexanone:

Cyclohexanone is a six-carbon cyclic molecule with a ketone functional group. It is a colorless, oily liquid (less dense than water) with an acetone-like smell.



It also known as oxo cyclohexane, pimelic ketone, ketohexamethylene, cyclohexyl ketone or ketocyclohexane.

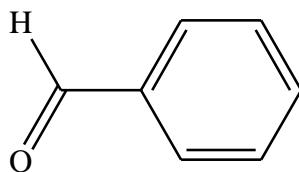
Cyclohexanone is occasionally found as a volatile component of human urine. Biological fluids such as blood and urine have been shown to contain a large number of components; some of them are volatiles (low boiling point) apparently present in all individuals, while others such are much more variable.

There is a strong correlation between the concentration of cyclohexanone in the working environment and its concentration in urine. Cyclohexanone is obtained through oxidation of cyclohexane or dehydrogenation of phenol. It is used in a large scale for the production of nylon.

Benzaldehyde:

Benzaldehyde (C_6H_5CHO) is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde .

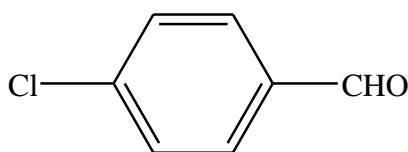
It is a colorless liquid with a characteristic almond-like odor. Benzaldehyde is the primary component of bitter almond oil and can be extracted from a number of other natural sources. Synthetic benzaldehyde is the flavoring agent in imitation almond extract, which is used to flavor cakes and other baked goods.

***p*-Chlorobenzaldehyde:**

p-chlorobenzaldehyde is a substituted aromatic benzaldehyde. It is a white to pale yellow powder which melt at 46°C and stable in normal condition but it is air and light sensitive.

The molecular weight is 140.57.

It is insoluble in water, easily soluble in alcohol, ether and benzene and soluble in acetone. It can be evaporated together with the steam.

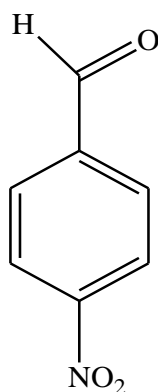


p-chlorobenzaldehyde is used as the intermediates of medicine and dyes, for the manufacturing of chlormezanone, dapsone aminobutyric acid and so on. It can be used for producing the plant growth regulator paclobutrazol.

p-Chlorobenzaldehyde is also used as an intermediate for the manufacture of dyestuffs, optical brighteners, pharmaceuticals, agricultural chemicals and metal finishing products.

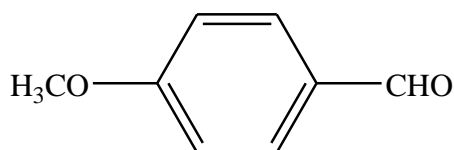
***p*-Nitrobenzaldehyde**

p-Nitrobenzaldehyde is an organic aromatic compound containing a nitro group para-substituted to an aldehyde. Its chemical formula is C₇H₅NO₃ and Melting point is 103 to 106 °C.



***p*-Methoxybenzaldehyde**

p-Anisaldehyde also known as anisic aldehyde or anise aldehyde is an organic compound that is commonly encountered in fragrances, both synthetic and natural. It is also known as *p*-methoxybenzaldehyde or *p*-methoxybenzaldehyde. The compound consists of a benzene ring with an aldehyde and a methoxy group. It is a clear liquid with a strong aroma.



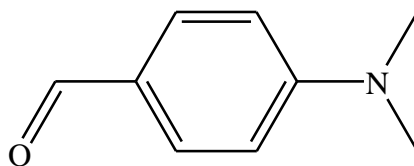
p-methoxybenzaldehyde or *p*- anisaldehyde is an interesting compound which is used in the field of medicine. It plays an important role in preparation of various drugs. Drugs made from *p*-anisaldehyde includes:

1. PMA & PMMA
2. 4-Hydroxyamfetamine
3. Dasantafil
4. Tomoxiprole
5. Benzestrol
6. Meobentine (via *p*-methoxybenzylamine made via reduction of the oxime).
7. Ambucetamide
8. Metostilenol

N, N-Dimethylaminobenzaldehyde

N,N-Dimethylaminobenzaldehyde is an organic compound containing amine and aldehyde moieties which is used in Ehrlich's reagent and Kovac's reagent to test for indoles. Ehrlich's reagent acts as a strong electrophile which reacts with the electron-rich α -carbon (2-position) of indole rings to form a blue-colored adduct.

The carbonyl group typically reacts with the electron rich 2-position of the indole but may also react at the C-3 or N-1 positions. It may also be used for determination of hydrazine as same as indole by forming azo dye which show yellow color.



3.2 Experimental Techniques Employed

Chromatographic Technique (Thin layer chromatography):

Chromatography is a separation process, which depend on the differential distributions of the component of a mixture between a mobile bulk phase and an essentially thin film stationary phase according to their polarity.

When this stationary phase remain in the form of a thin layer adhering to a suitable form of backing material over which the mobile phase is allow to ascent by capillary action, the technique is called thin layer chromatography (TLC).

The most commonly used stationary phases, which are available in different grades specially prepared for TLC use, include silica gel, alumina, kieselguhr and cellulose powders.

Preparation of plates

In this technique the glass plates were cleaned by detergent to remove the greasy material and then dried. The plates were coated with silica gel.

The TLC plates (2.5 cm× 6.0 cm) were prepared by dipping the plates into slurry made of UV active silica gel.



Fig 3.1 Prepared TLC Plate

The plates were activated by heating at 150°C for 10-12 hours in an oven to remove moisture. Cylindrical glass chamber (TLC tank) was used for the development of chromatoplates. The selected solvent system was poured in sufficient quantity into the tank. A smooth sheet of filter paper was introduced into the tank and allowed to soak in the solvent. The tank was then made airtight and kept for few minutes to saturate the internal atmosphere with the solvent vapor.

A small amount of dried extract was dissolved in a suitable solvent to get a solution (approximately 1%). A small spot of the solution was applied on the activated silica plate with a capillary tube just 1 cm above the lower edge of the plate (base line). The spot was dried with a hot air blower and a straight line was drawn 2 cm below the upper edge of the activated plate which marks the upper limit (solvent front) of the solvent flow. The spotted plate was then placed in the tank (n-hexane: ethyl acetate = 60:40) in such a way as to keep the applied spot above the surface of the solvent system and the cap was placed again. The plate was left for development.

When the solvent front reaches up to the given mark, the plate was taken out and air-dried. The properly developed plates were kept in an iodine chamber for 10-15 minutes and viewed the spot travelled by the compound. By measuring the distance travelled by the solute and solvent the R_f value was calculated.

Application of sample on the plate:

Sample was applied to thin layer by capillary tube. But considerably more skill and care are needed so that a hole was not produced on the film.

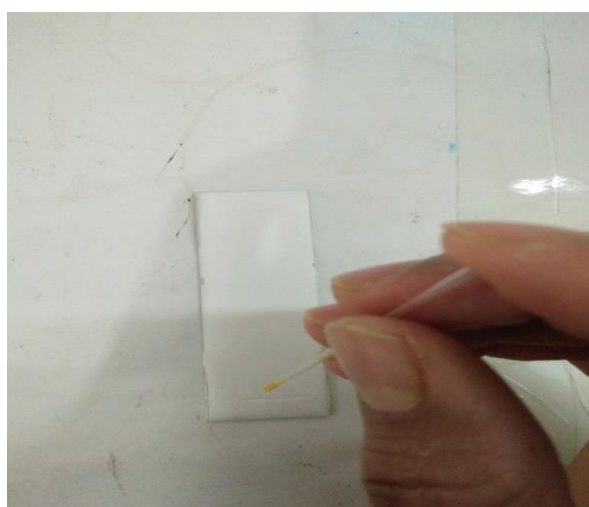


Fig 3.2 process of spotting

Solvent Systems

The solvents of different polarity used for TLC are given below:

- a. n-hexane
- b. n-hexane : Ethyl acetate (in different ratio)
- c. Ethanol (EtOH)

Development of plates:

When the sample was spotted on the film of plates, it was developed in ascending process. Usually plates were placed in a tank. The plates were put in such a way that they were inclined and the lower edge immersed in the selected mobile phase, but the solvent barrier was somewhat below than the starting line (base line).

Location of Spots:

Detection of compounds in TLC plates was a very important topic in analyzing extractives to isolate pure compounds. The following technique was used for detecting the compounds in TLC plates.

Iodine chamber

The developed chromatogram was placed in a closed chamber containing crystals of iodine and kept for few minutes. The compounds that appeared as yellow spots were marked. Unsaturated compounds absorb iodine. Bound iodine is removed from the plate by air blowing.



Fig 3.3 Iodine Chamber

The R_f value:

The retarding factor (R_f value) of any compound seen on a TLC plate was calculated according to the following equation

$$R_f = \frac{\text{Distance (cm) traveled by solute}}{\text{Distance (cm) traveled by solvent}}$$

Recrystallization:

Crystallization was employed as a final purification process. The solvent in which the compound was dissolved in a minimum volume of solvent in normal condition and was left undisturbed for crystallization. Sometimes mixtures of solvents were used.



Fig 3.4 Process of evaporation

The compound was dissolved in a suitable solvent and then a solvent in which the compound was insoluble. The solvent with comparatively lower polarity was gradually added until cloudiness developed in the solution.

3.3 Spectroscopic Techniques:

Ultraviolet and visible spectra:

Ultra violet and visible spectra of the sample were recorded on UV-1800 SHIMADZU Spectrophotometer, ultraviolet spectrometer with a scanning range of 800-220 nm. The spectra were run by using Ethanol, Ethyl acetate and DCM as solvents.



Fig 3.5 UV-Vis spectrophotometer

3.5

Infra-red-spectra: Infra-red spectra of the samples were recorded on the IRTracer-100 (FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER) SHIMADZU.



Fig 3.6 IR Spectrophotometer

The spectra for solid samples were recorded as KBr pellets.

¹H NMR spectra:

¹H NMR spectra of the sample were recorded on a 500 MHz NMR spectra. The solvent used was CDCl₃. TMS was used as an internal standard.

Abbreviation Used

UV	Ultraviolet
IR	Infra-red
NMR	Nuclear magnetic resonance.
S	Singlet
Bs	Broad single
D	Doublet
M	Multiplet
<i>J</i>	Coupling constant
TLC	Thin Layer Chromatography
R _f	Retarding factor
Bp	Boiling point
Hz	Hertz
δ	Chemical shift
TMS	Tetra methyl Silane
D ₆	Deuterated Dimethylsulfoxide

Evaporation

All evaporations were carried under reduced pressure using rotary vacuum evaporator; the bath temperature was not exceeding 40°-50° C.

Melting point apparatus

Melting point (m.p) was determined by using an electro thermal melting point apparatus (Stuart, Melting point SPM 30).

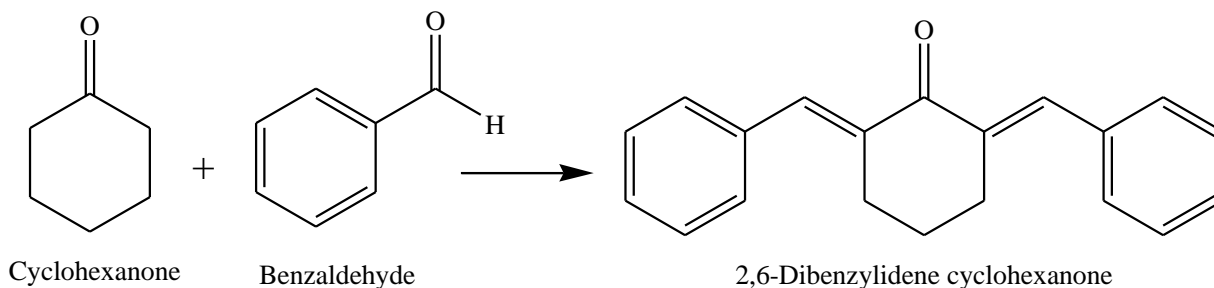


Fig 3.7 Melting point determination

3.4 Preparation of substituted bis-chalcones

Preparation of 2,6 Dibenzylidene-cyclohexanone

A mixture of 1.03 ml, 1 eq cyclohexanone, 2.03 ml, 2 eq pure benzaldehyde, and 0.88 g, 2.2 eq solid NaOH was ground in a mortar and pestle for 20 minutes at RT and then dilute HCl was poured in the reaction mixture. The separated solid material was filtered and dried. The solid obtained was purified by re-crystallization from ethanol and ethyl acetate mixture. The R_f value of the compound **1** was 0.56 (n-hexane : ethyl acetate = 3: 2). The percentage of yield of the product was 94%.

Reaction scheme**Characterization and structure determination of the product**

The product of the color was yellow crystal and the melting point of the pure product was 106⁰C.

Chemical test

The obtained product **1** gave red color ppt on treatment with 2,4-Dinitrophenyl hydrazine which indicates the presence of carbonyl group.

Spectral properties**UV spectrum**

The UV spectrum of the product **1** in EtOH exhibited λ_{\max} at 330 nm .

IR Spectrum

The IR spectrum of the product **1** run as KBr pellet exerted absorption band ν in cm⁻¹ which was assigned as: 3022, 2950, 2933, 1661, 1574, 1443, 1434.

¹H NMR Spectrum

The ¹H NMR spectrum of the compound in CDCl₃ gave the following signals value) using TMS as an internal standard.

¹H NMR (400MHz, CDCl₃) δ : 7.80, 7.47, 7.41, 7.34, 2.93, 1.82-1.76.

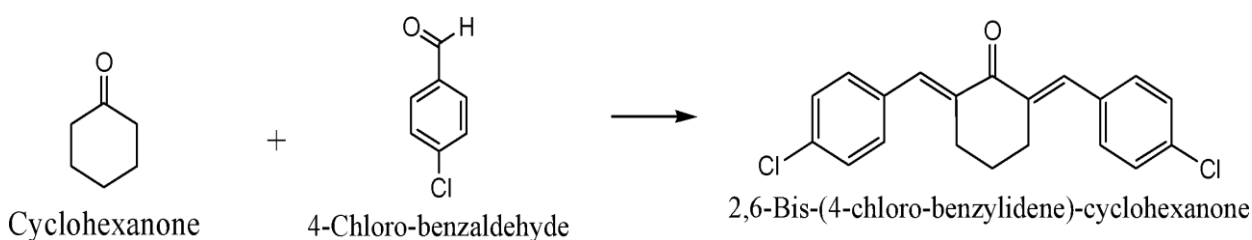
3.1.8 Preparation of 2,6-Bis-(4-chloro-benzylidene)-cyclohexanone

A mixture of 0.518 ml, 1 eq cyclohexanone, 1.41 g, 2 eq *p*-chlorobenzaldehyde and 0.44g, 2.2 eq solid NaOH was ground in a mortar and pestle for 20 minutes at RT and then dilute HCl was poured in the reaction mixture.

The separated solid material was filtered and dried. The solid obtained was purified by re-crystallization from ethanol and ethyl acetate mixture.

The R_f value of the compound **2** was 0.45 (n-hexane : ethyl acetate = 3: 2). The percentage of yield of the product was 89%.

Reaction scheme



Characterization and structure determination of the product

The product of the color was yellowish green and the melting point of the pure product was 124⁰C.

Chemical test

The obtained product **2** gave red color ppt. on treatment with 2,4-Dinitrophenyl hydrazine which indicates the presence of carbonyl group.

Spectral properties

UV-Visible spectrum

The UV spectrum of the product **2** in EtOH exhibited λ_{\max} at 333 nm.

IR Spectrum:

The IR spectrum of the product **2** run as KBR pellet asserted absorption band ν in cm^{-1} which was assigned as:

2964, 2927, 1667, 1585, 1576, 1465, 1265, 1160, 821, 800.

¹H NMR

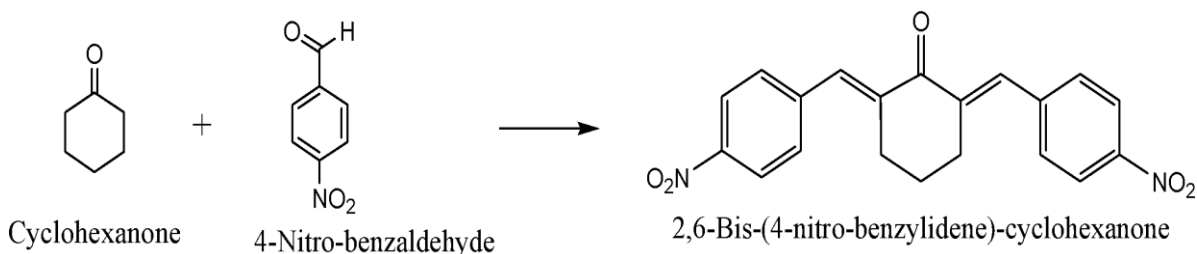
The ¹H NMR spectrum of the compound **2** in CDCl₃ gave the following signals (δ value) using TMS as an internal standard.

¹H NMR (400MHz, CDCl₃) δ: 7.73, 7.38-7.25, 2.91-2.87, 1.84-1.77.

3.1.9 Preparation of 2,6-Bis-(*p*-nitro-benzylidene)-cyclohexanone

A mixture of 0.32 ml, 1 eq cyclohexanone, 0.997g, 2 eq *p*-nitrobenzaldehyde and 0.29 g, 2.2 eq solid NaOH was ground in a mortar and pestle for 20 minutes at RT and then dilute HCl was poured in the reaction mixture. The separated solid material was filtered and dried. The solid obtained was purified by re-crystallization from ethanol and ethyl acetate mixture. The R_f value of the compound **3** was 0.79 (n-hexane : ethyl acetate = 3: 2). The percentage of yield of the product was 91%.

Reaction scheme



Characterization and structure determination of the product

The product of the color was light brown and the melting point of the pure product was 172^oC.

Chemical test

The obtained product **3** gave red color ppt. on treatment with 2,4-Dinitrophenyl hydrazine which indicates the presence of carbonyl group.

Spectral properties

UV-Visible spectrum

The UV spectrum of the product **3** in EtOH exhibited λ_{\max} at 340 nm.

IR Spectrum

The IR spectrum of the product **3** run as KBR pellet asserted absorption band ν in cm^{-1} which was assigned as: 2923, 2850, 1669, 1599, 1517, 1491, 1345, 1300, 1268, 1160.

^1H NMR

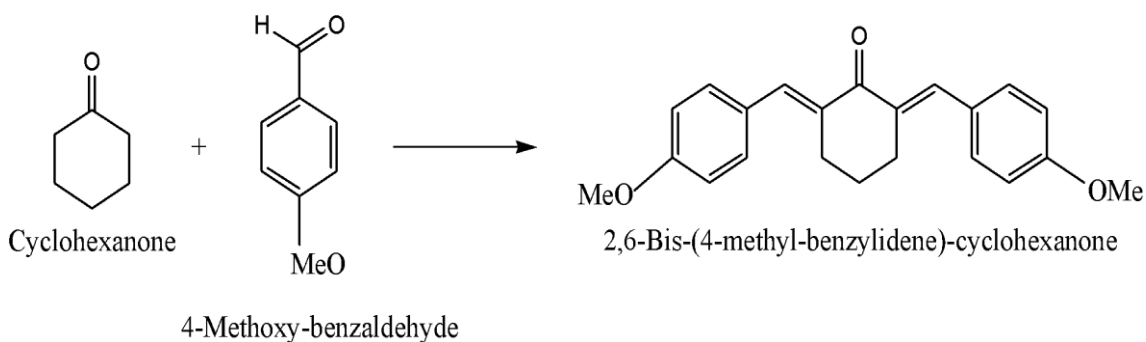
The ^1H NMR spectrum of the compound **3** in DMSO gave the following signals (δ value) using TMS as an internal standard.

^1H NMR (400MHz CDCl_3) δ : 8.24, 7.81, 7.59, 2.94, 1.88-1.82.

preparation of 2,6-Bis-(*p*-methoxy-benzylidene)-cyclohexanone

A mixture of 0.52 ml, 1 eq cyclohexanone, 1.21 ml, 2 eq *p*-methoxybenzaldehyde and 0.44 g, 2.2 eq solid NaOH was ground in a mortar (where the basic NaOH is act as a catalyst) and pestle for 20 minutes at RT and then dilute HCl was poured in the reaction mixture. The separated solid material was filtered and dried. The solid obtained was purified by re-crystallization from ethanol and ethyl acetate. The R_f value of the compound **4** was 0.72 (n-hexane : ethyl acetate = 3: 2). The percentage of yield of the product was 83%.

Reaction schem



Characterization and structure determination of the product

The product of the color was pale yellow and the melting point of the pure product was 152⁰ C.

Chemical test

The obtained product **4** gave red color ppt. on treatment with 2,4-Dinitrophenyl hydrazine which indicates the presence of carbonyl group.

Spectral properties**UV-Visible spectrum**

The UV spectrum of the product **4** in EtOH exhibited λ_{\max} at 359 nm.

IR Spectrum

The IR spectrum of the product **4** run as KBR pellet asserted absorption band ν in cm^{-1} which was assigned as: 2938, 2827, 1657, 1595, 1199, 1184, 870, 837.

¹H NMR

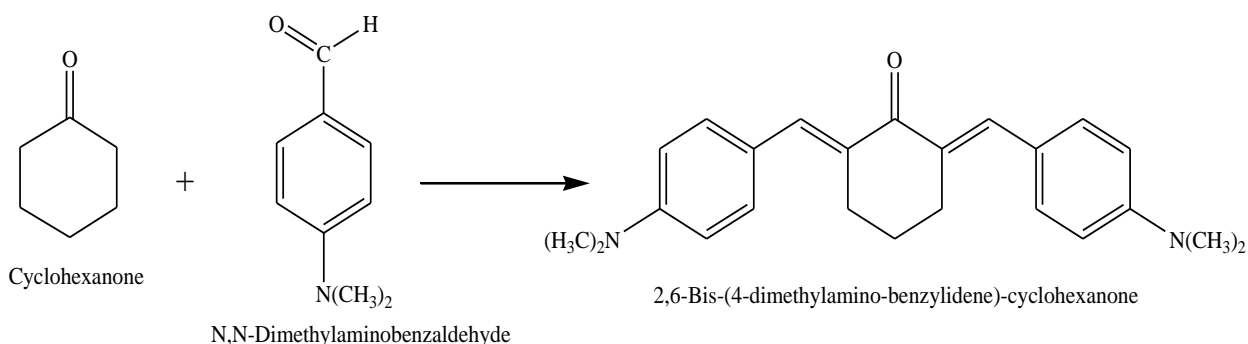
The ¹H NMR spectrum of the compound in DMSO gave the following signals (δ value) using TMS as an internal standard.

¹H NMR (400MHz CDCl₃) δ : 7.76, 7.45, 6.93, 3.85, 2.92, 1.84-1.78.

Preparation of 2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone

A mixture of cyclohexanone 0.32 ml, 1 eq; N,N-dimethyl amino benzaldehyde 0.98 g, 2 eq and solid NaOH 0.29 g, 2.2 eq was ground in a mortar and pestle for 20 minutes at RT and then dilute HCl was poured in the reaction mixture.

The separated solid material was filtered and dried. The solid obtained was purified by re-crystallization from ethanol and ethyl acetate mixture. The R_f value of the compound **5** was 0.58 (n-hexane : ethyl acetate = 3: 2). The percentage of yield of the product was 79%.

Reaction scheme**Characterization and structure determination of the product**

The product of the color was yellow and the melting point of the pure product was 136 °C.

Chemical test

The obtained product **5** gave red color ppt. on treatment with 2,4-Dinitrophenyl hydrazine which indicates the presence of carbonyl group.

Spectral properties**UV-Visible spectrum**

The UV spectrum of the product **5** in EtOH exhibited λ_{\max} at 452 nm.

IR Spectrum

The IR spectrum of the product **5** run as KBR pellet showed absorption band ν_{\max} in cm^{-1} which was assigned as: 2926, 2853, 1645, 1609, 1361, 1302, 1157, 871, 818.

 ^1H NMR

The ^1H NMR spectrum of the compound **5** in DMSO gave the following signals (δ value) using TMS as an internal standard.

^1H NMR (400MHz CDCl_3) δ : 7.76, 7.45, 6.71, 3.01, 2.94, 1.83 -1.79.

CHAPTER 4

Results and discussion

CHAPTER 4

Results and discussion

4.1 Reaction of benzaldehyde with cyclohexanone:

The reaction of benzaldehyde with cyclohexanone in presence of NaOH at room temperature gave a yellow crystalline solid **1**, m.p.106° C. The R_f value of the product was found to be 0.56 [eluting solvent; n-hexane : ethyl acetate = 60:40]. The yield of the product was 94%.

Spectral properties

UV spectrum

The UV spectrum of the compound **1** in EtOH

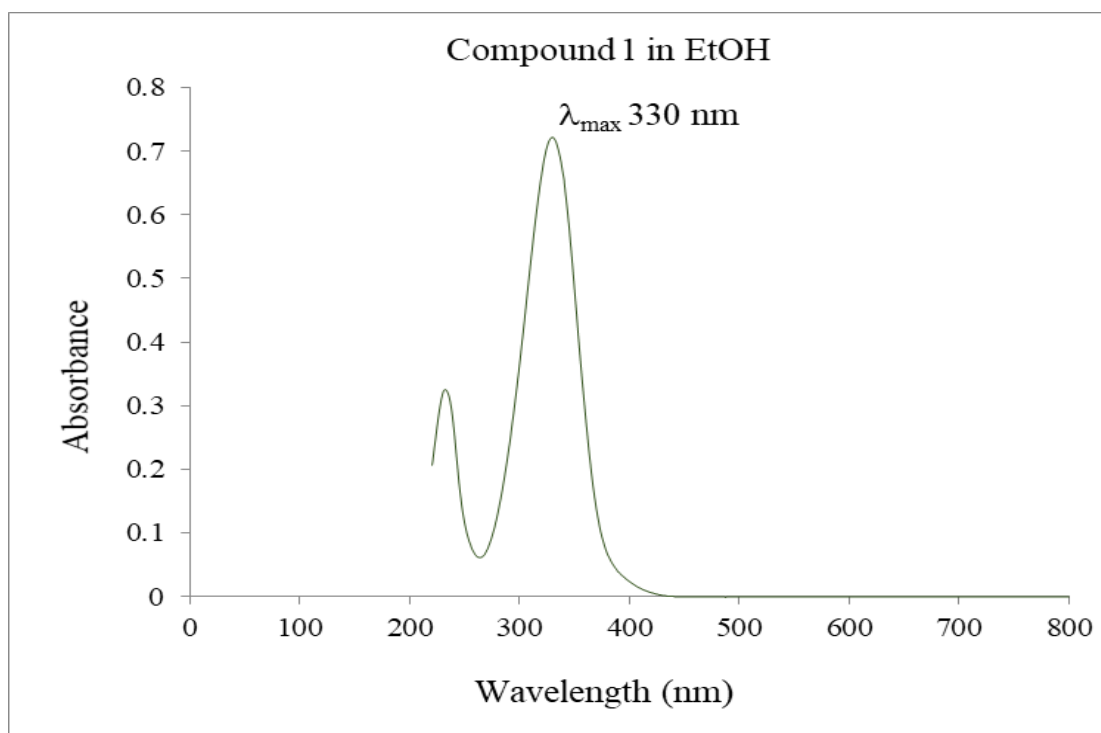


Fig 4.1 UV spectrum of compound **1** in EtOH

IR spectrum

Table 4.1: IR value of compound 1

Absorption bands, ν in cm^{-1}	Group present
3022, 2950, 2933	C-H stretching in aromatic
1661	C=O in conjugation with C=C
1574	C=C in conjugation with C=O and C=C

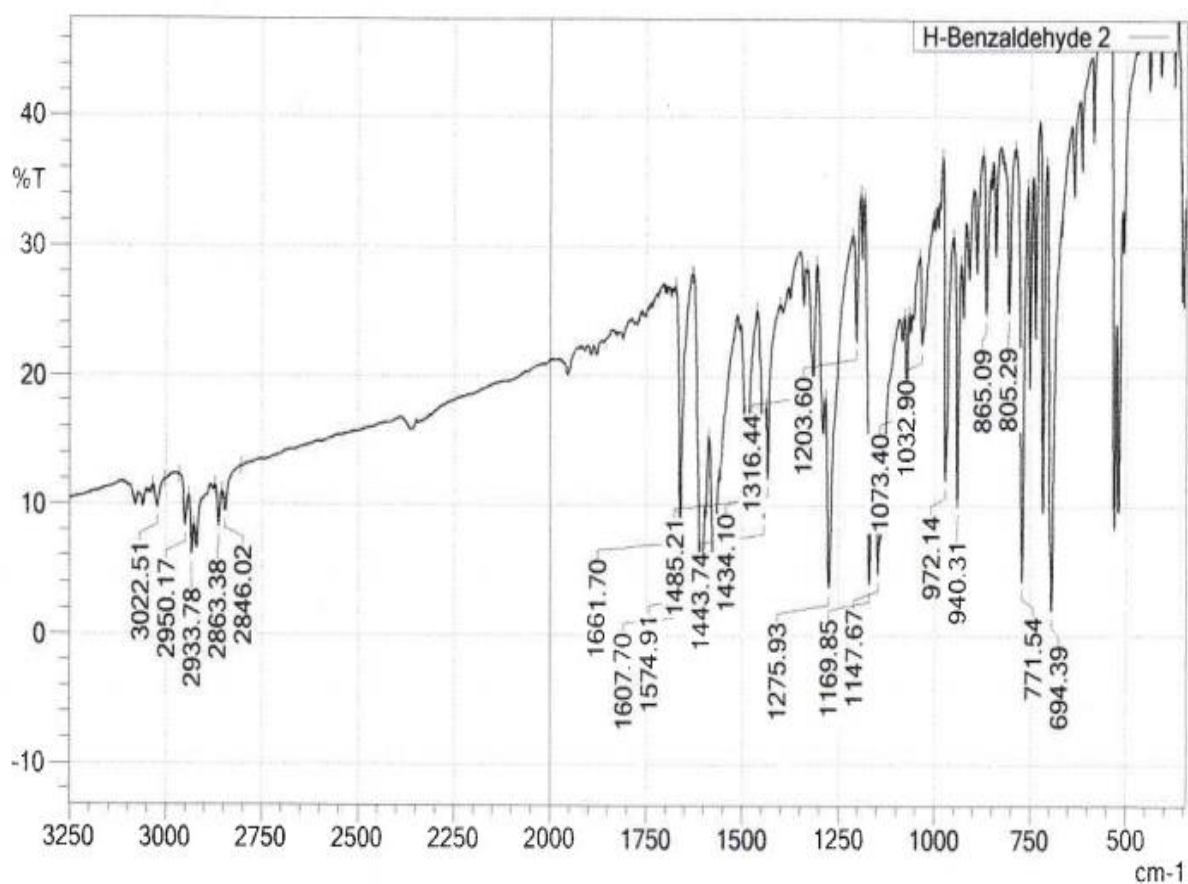


Fig. 4.2 IR spectrum of compound 1

¹H NMR spectrum

The ¹H NMR spectrum of the compound **1** in CDCl₃ gave the following signals (δ value) using TMS as an internal standard.

¹H NMR (400MHz CDCl₃) δ=7.80 (s, 2H, Allylic) 7.47 (d, *J* = 7.4 Hz, 4H, Ar), 7.41 (t, *J*=14.7 Hz, 4H, Ar), 7.34 (t, *J*=14.4 Hz, 2H, Ar), 2.93 (t, *J*= 14.4 Hz, 4H, 2 × CH₂), 1.82-1.76 (m, 2 H, CH₂).

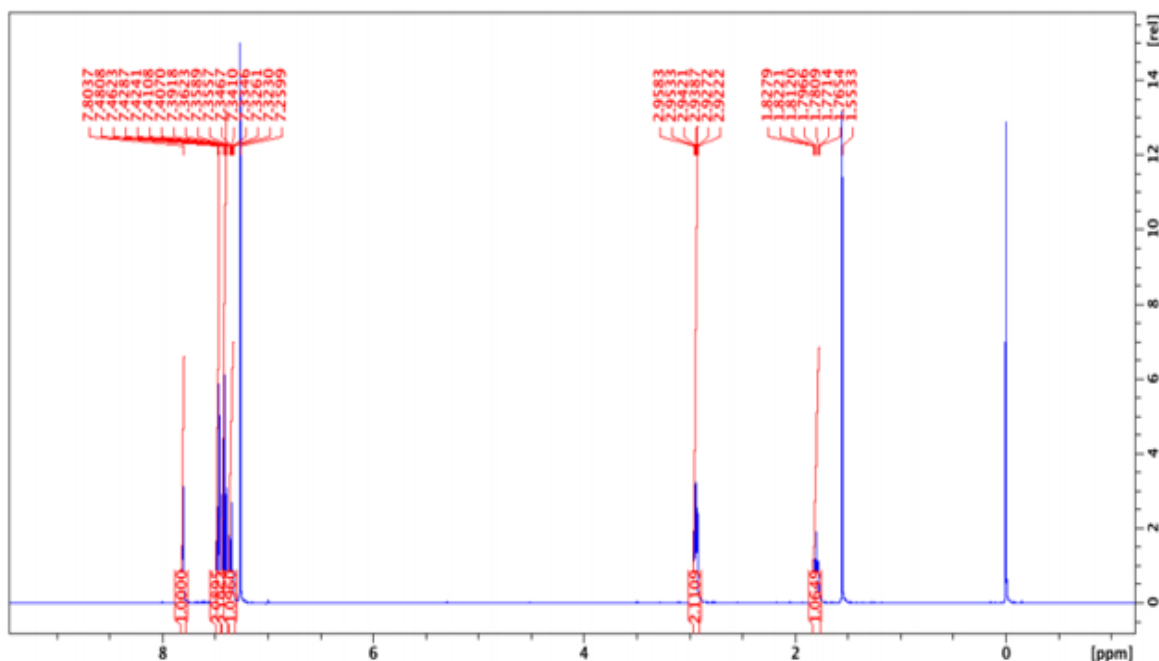
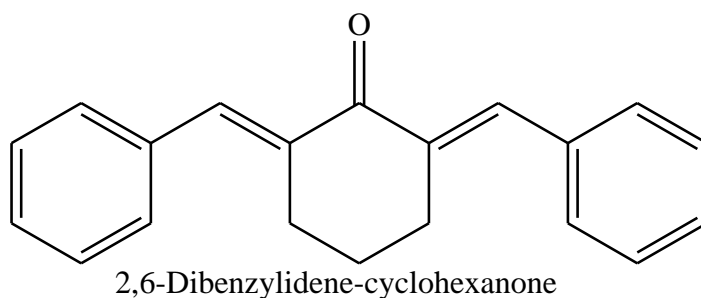


Fig: 4.3 ¹H NMR spectrum of compound **1**

On the basis of the spectral properties (UV, IR & ¹H NMR) and chemical behavior, the following structure has been assigned to the obtained product.



1

4.2 Reaction of *p*-chlorobenzaldehyde with cyclohexanone:

The reaction of *p*-chlorobenzaldehyde with cyclohexanone in presence of NaOH at room temperature gave a yellowish green product **2**, m.p.124° C.

The R_f value of the product was found to be 0.45 [eluting solvent ; n-hexane : ethyl acetate = 60:40]. The yield of the product was 89%.

Spectral properties

UV spectrum

The UV spectrum of the compound **2** in EtOH

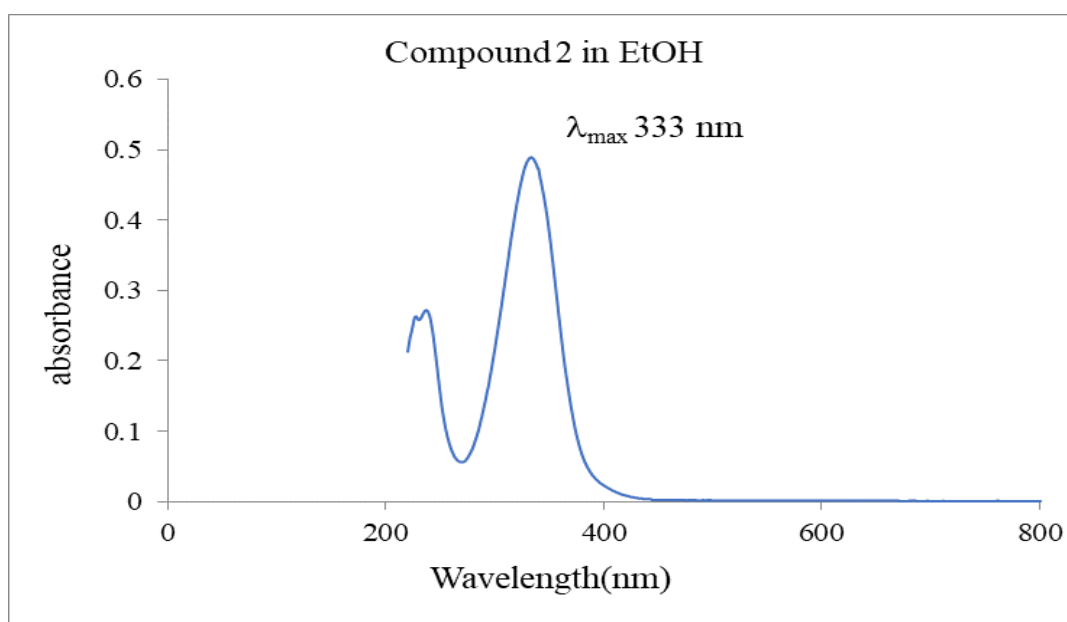


Fig 4.4 UV spectrum of compound **2** in EtOH

IR spectrum

Table 4.2 IR value of compound **2**

Absorption bands, ν in cm^{-1}	Group present
2964,2927	C-H stretching in aromatic
1667	C=O in conjugation with C=C

1585, 1576	C=C in conjugation with C=O and C=C
821, 800	C-Cl stretching in aromatic

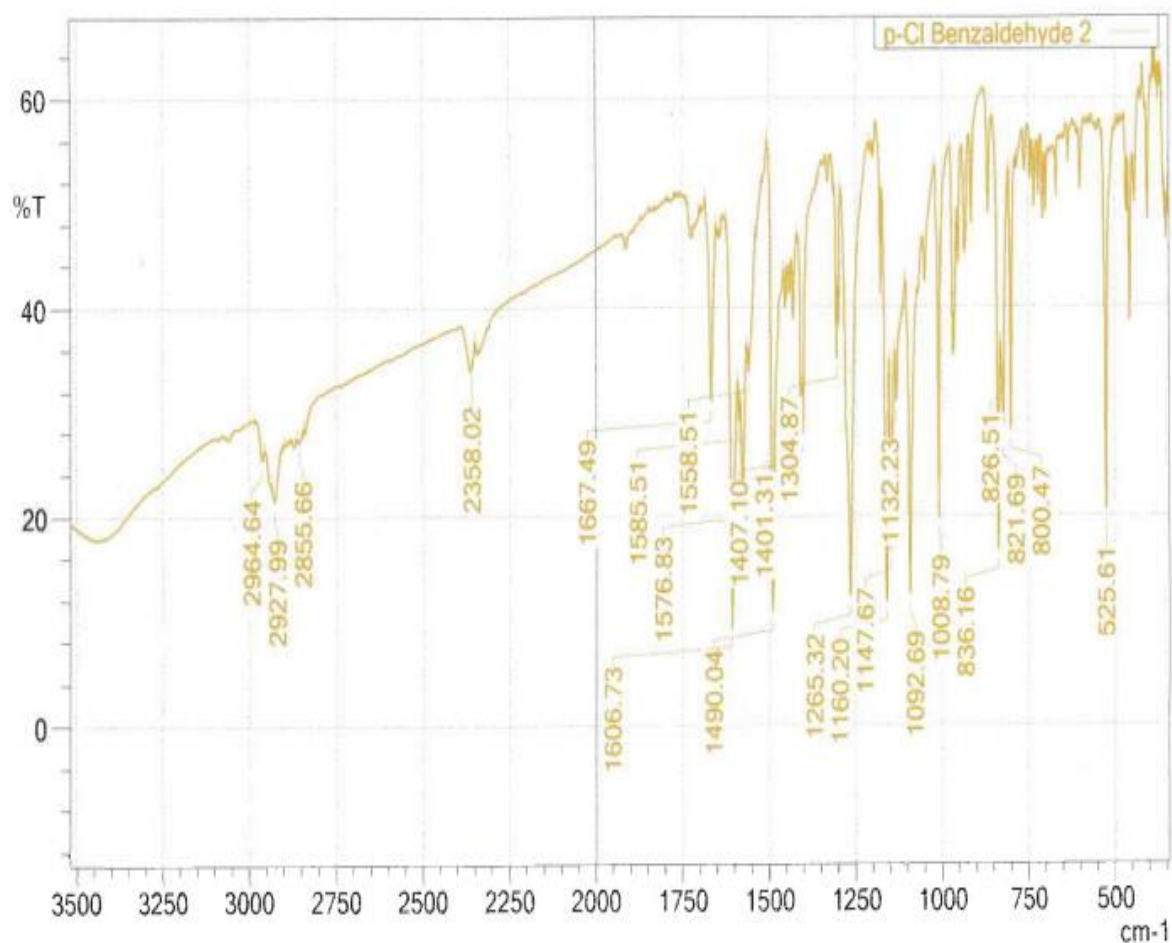


Fig 4.5 IR spectrum of compound 2

¹H NMR spectrum

The ¹H NMR spectrum of the compound 2 in CDCl₃ gave the following signals (δ value) using TMS as an internal standard.

^1H NMR (400MHz CDCl_3) δ =7.73 (s, 2H, Allylic) 7.38-7.25(m, 8H, Ar), 2.91-2.87 (m, 4H, $2 \times \text{CH}_2$), 1.84-1.77 (m, 2H, CH_2).

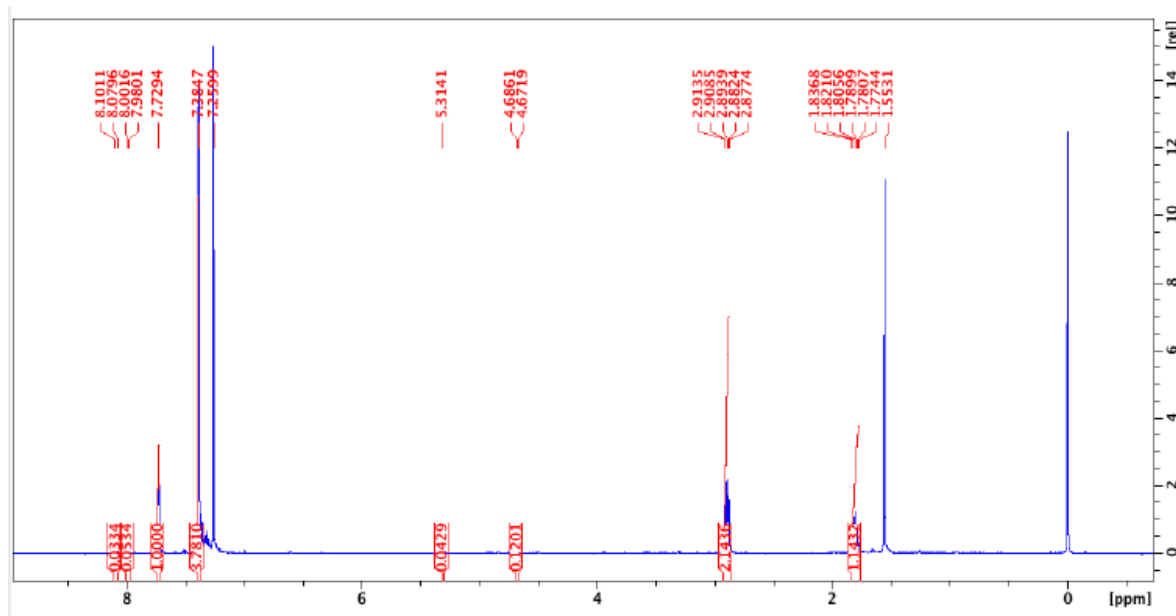
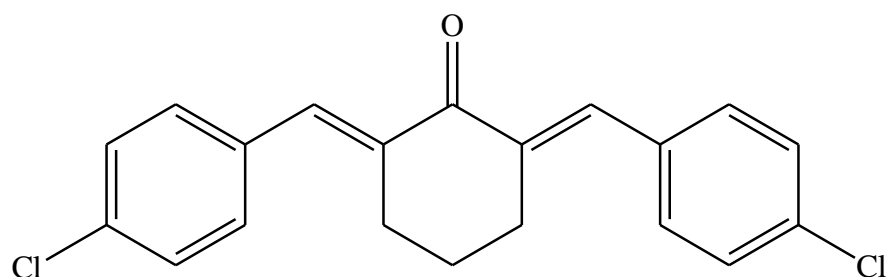


Fig: 4.6 ^1H NMR spectrum of compound **2**

On the basis of the spectral properties (UV, IR & ^1H NMR) and chemical behavior, the following structure has been assigned to the obtained product.



2,6-Bis-(4-chloro-benzylidene)-cyclohexanone

2

4.3 Reaction of *p*-nitrobenzaldehyde and cyclohexanone

The reaction of *p*-nitrobenzaldehyde and cyclohexanone in presence of NaOH gave a light brown crystalline solid **3**, m.p.172° C. The R_f value of the product was found to be 0.79 [eluting solvent; n-hexane : ethyl acetate= 60:40]. The yield of the product was 91%.

Spectral properties

UV spectrum

The UV spectrum of compound **3** in EtOH

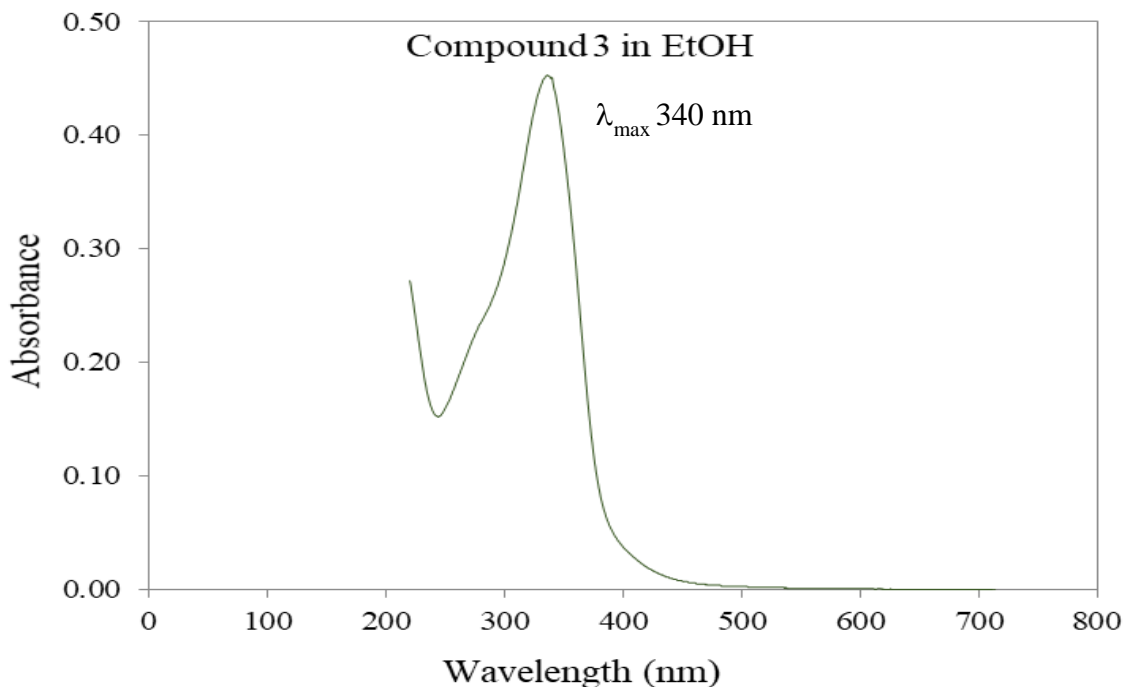


Fig 4.7 UV spectrum of compound **3** in EtOH

IR spectrum

Table 4.3 IR value of compound **3**

Absorption bands, ν in cm^{-1}	Group present
2923,2850	C-H stretching in aromatic
1669	C=O in conjugation with C=C
1599	C=C in conjugation with C=O and C=C
1517,1491	NO ₂ in aromatic
1345,1300	C-N stretching in aromatic

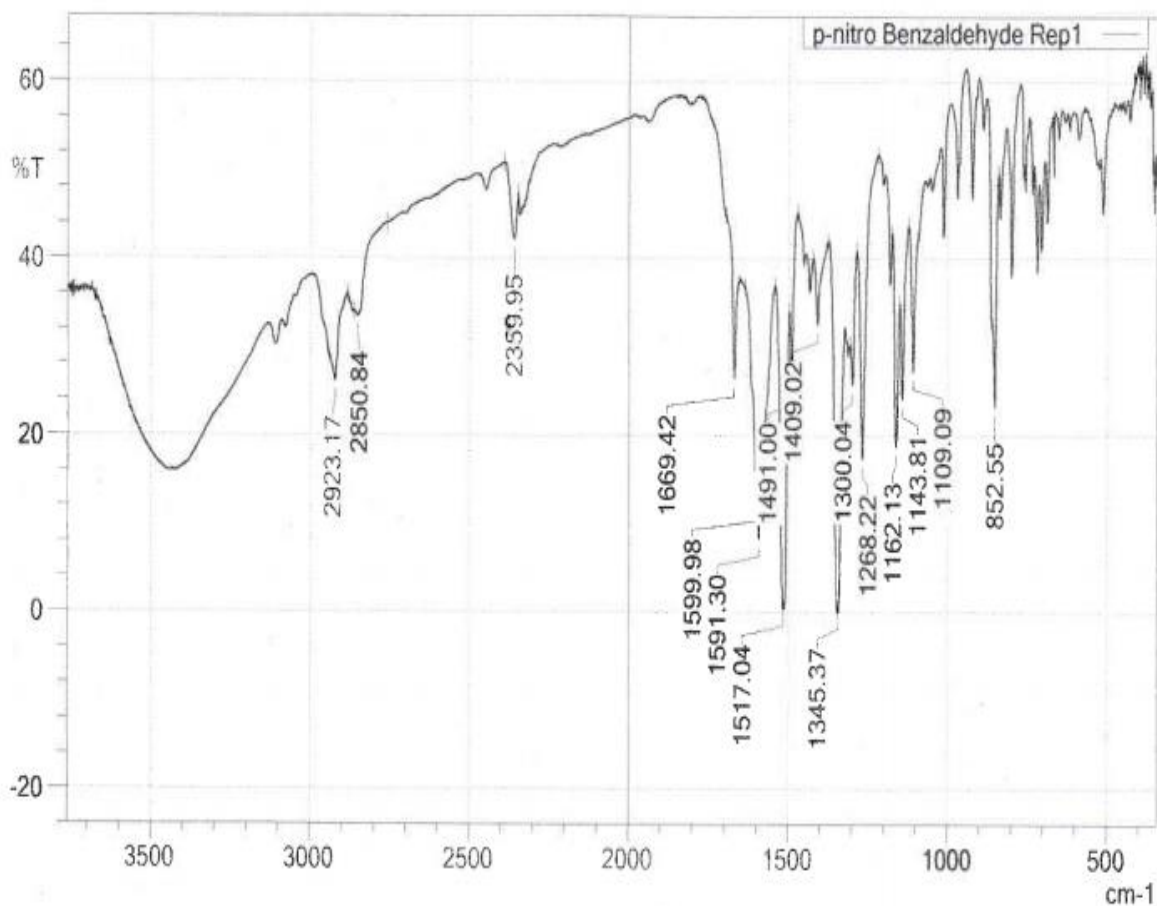


Fig 4.8 IR spectrum of compound **3**

¹H NMR spectrum

The ¹H NMR spectrum of the compound **3** in DMSO gave the following signals (δ value) using TMS as an internal standard.

¹H NMR (400MHz CDCl₃) δ =8.24 (d, J =8.7, 4H, Ar), 7.81(s, 2H, Allylic), 7.59 (d, J = 8.7 Hz, 4H, Ar), 2.94 (t, J = 10.3 Hz, 4H, 2 \times CH₂), 1.88-1.82 (m, 2H, CH₂).

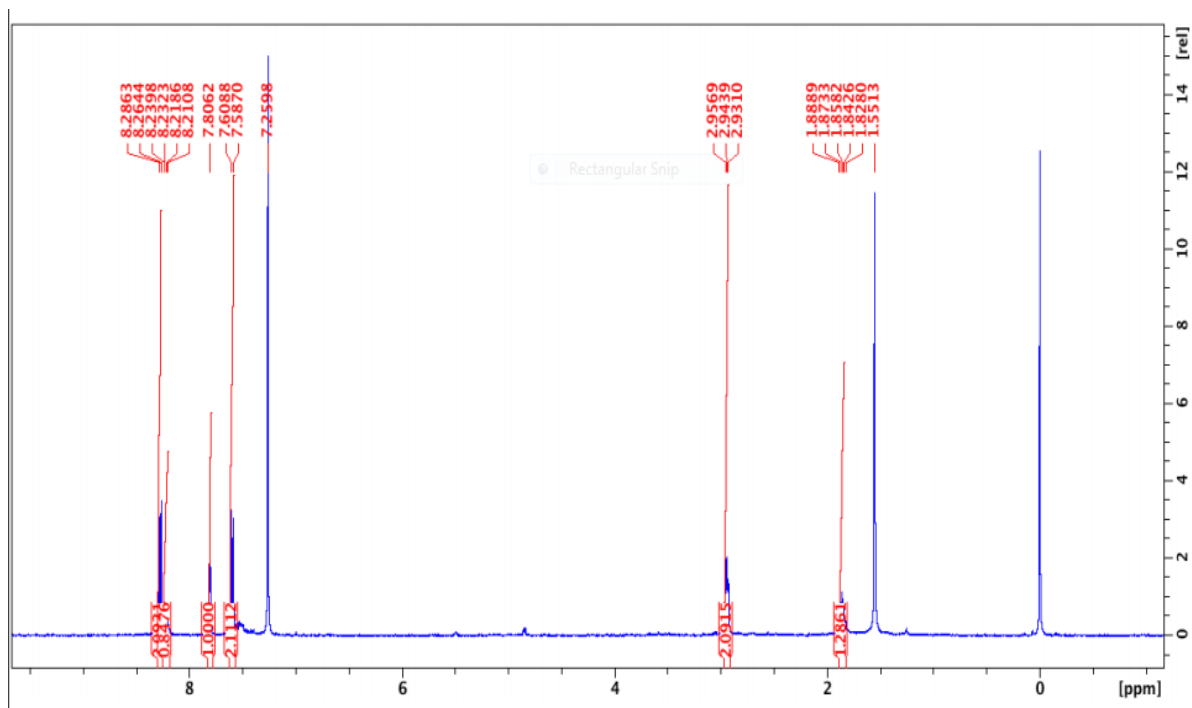
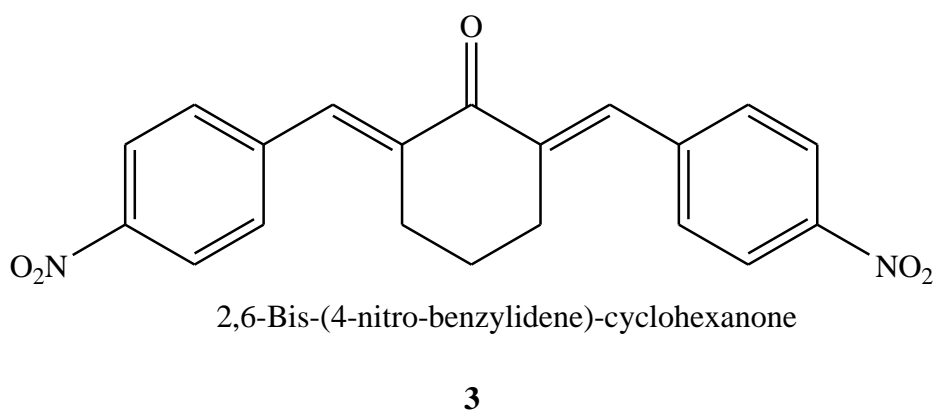


Fig: 4.9 ^1H NMR spectrum of compound **3**

On the basis of the spectral properties (UV, IR & ^1H NMR) and chemical behavior, the following structure has been assigned to the obtained product.



4.4 Reaction of *p*-methoxy benzaldehyde and cyclohexanone

The reaction of *p*-methoxy benzaldehyde and cyclohexanone in presence of NaOH gave a pale yellow solid **4**, m.p 152°C . The R_f value of the product was found to be 0.72 [eluting solvent; n-hexane : ethyl acetate = 60:40]. The yield of the product was 83%.

Spectral properties:**UV spectrum**

The UV spectrum of the product **4** in EtOH

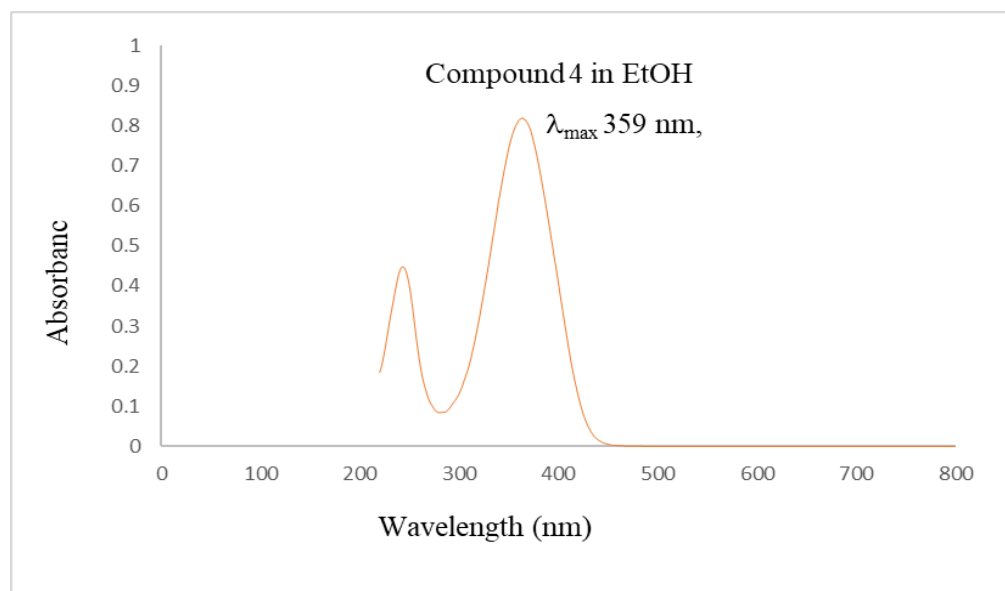


Fig 4.10 UV spectrum of compound **4** in EtOH

IR spectrum

Table 4.4 IR value of compound **4**

Absorption bands, ν in cm^{-1}	Group present
2938,2827	C-H stretching in aromatic
1657	C=O in conjugation with C=C
1595	C=C in conjugation with C=O and C=C

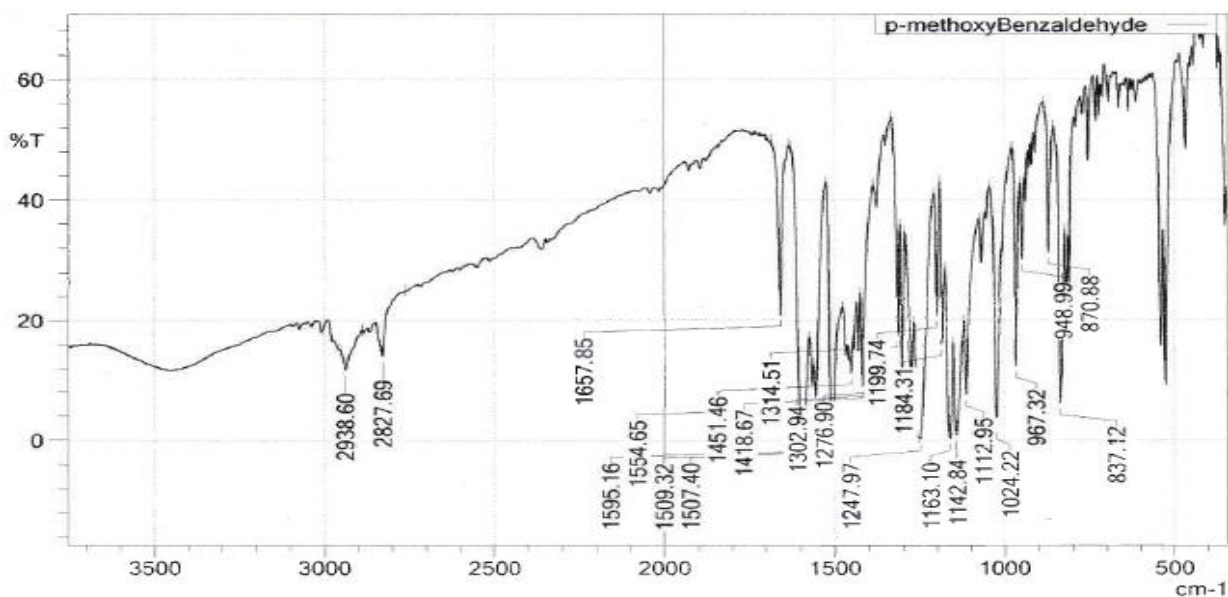
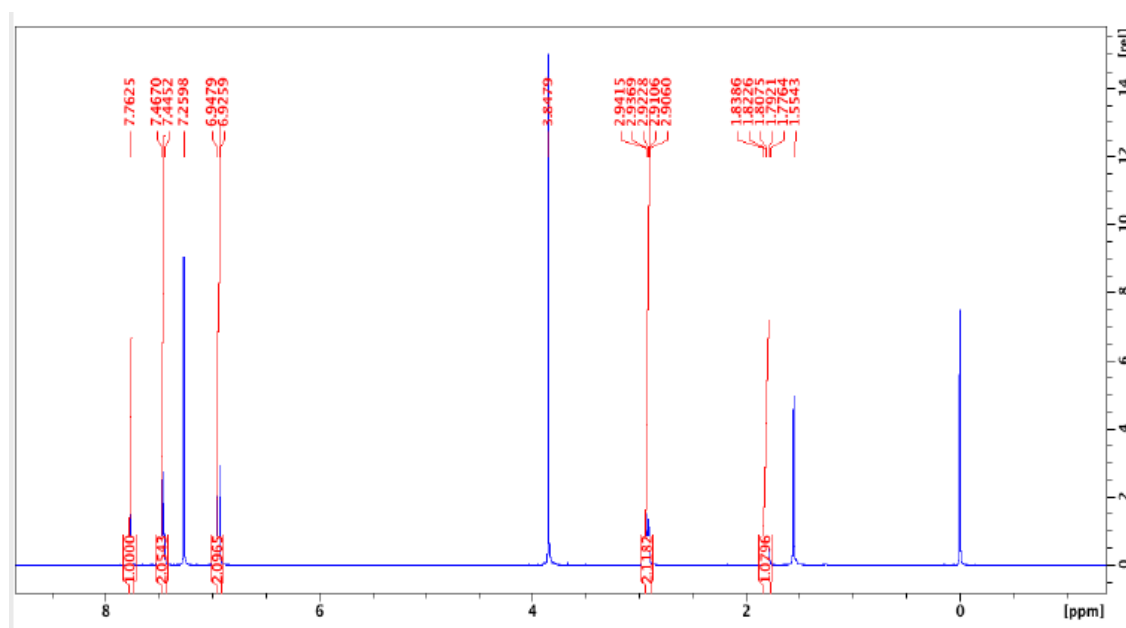


Fig 4.11 IR spectrum of compound 4

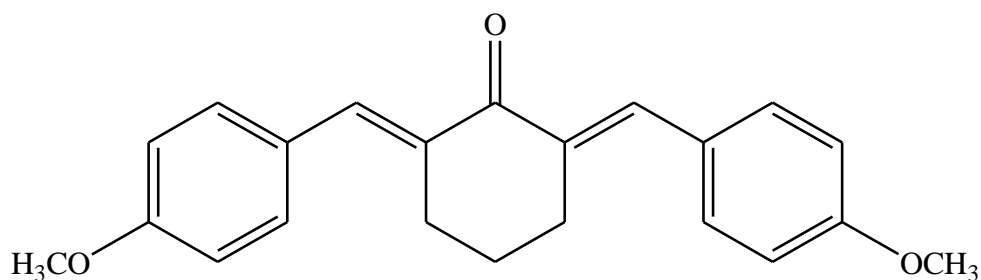
^1H NMR spectrum

The ^1H NMR spectrum of the compound in DMSO gave the following signals (δ value) using TMS as an internal standard.

^1H NMR (400MHz CDCl_3) $\delta=7.76$ (s, 2H, Allylic), 7.45 (d, $J = 8.7$ Hz, 4H, Ar), 6.93 (d, $J = 8.8$ Hz, 4H, Ar), 3.85 (s, 6H, $2 \times \text{CH}_3\text{O}$), 2.92 (t, $J = 14.2$, 4H, $2 \times \text{CH}_2$), 1.84-1.78 (m, 2H, CH_2).

Fig: 4.12 ^1H NMR spectrum of compound 4

On the basis of the spectral properties (UV, IR & ^1H NMR) and chemical behavior, the following structure has been assigned to the obtained product.



2,6-Bis-(4-methoxy-benzylidene)-cyclohexanone

4

4.5 Reaction of N,N-dimethyl amino benzaldehyde and cyclohexanone

The reaction of N,N-dimethyl amino benzaldehyde and cyclohexanone in presence of NaOH gave a yellow solid **5**, m.p 127°C . The R_f value of the product was found to be 0.58 [eluting solvent; n-hexane : ethyl acetate= 60:40]. The yield of the product was 79%.

Spectral properties:

UV spectrum

The UV spectrum of the product **5** in EtOH

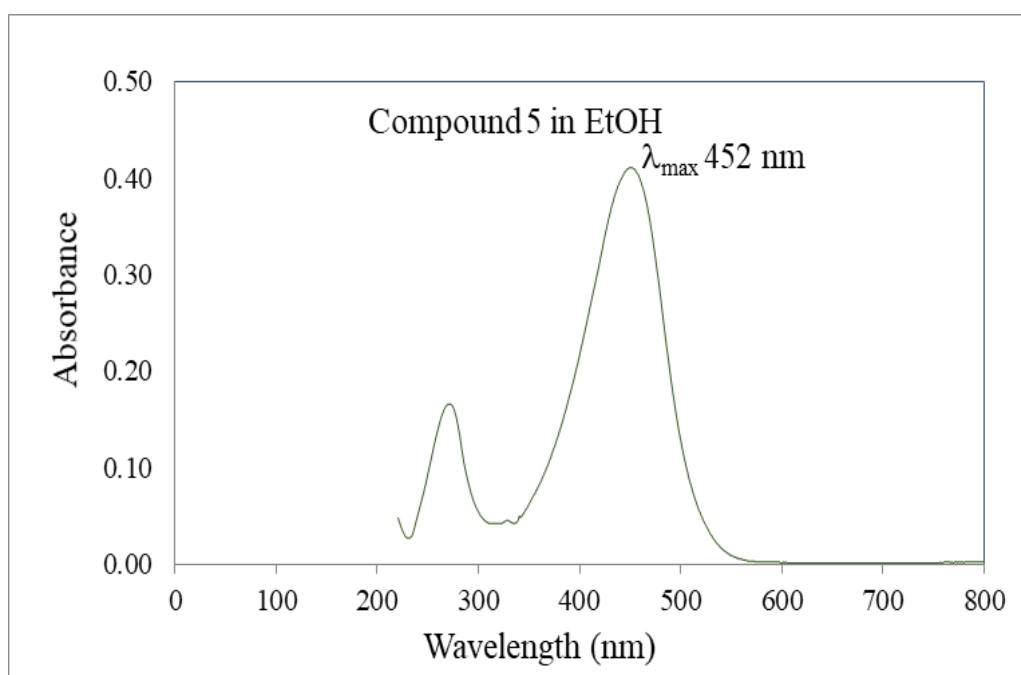


Fig 4.13 UV spectrum of compound **5** in EtOH

IR spectrum

Table 4.5 IR value of compound 5

Absorption bands, ν in cm^{-1}	Group present
2926,2853	C-H stretching in aromatic
1645	C=O in conjugation with C=C
1609	C=C in conjugation with C=O and C=C stretching of phenyl
1361,1302	C-N stretching in aromatic

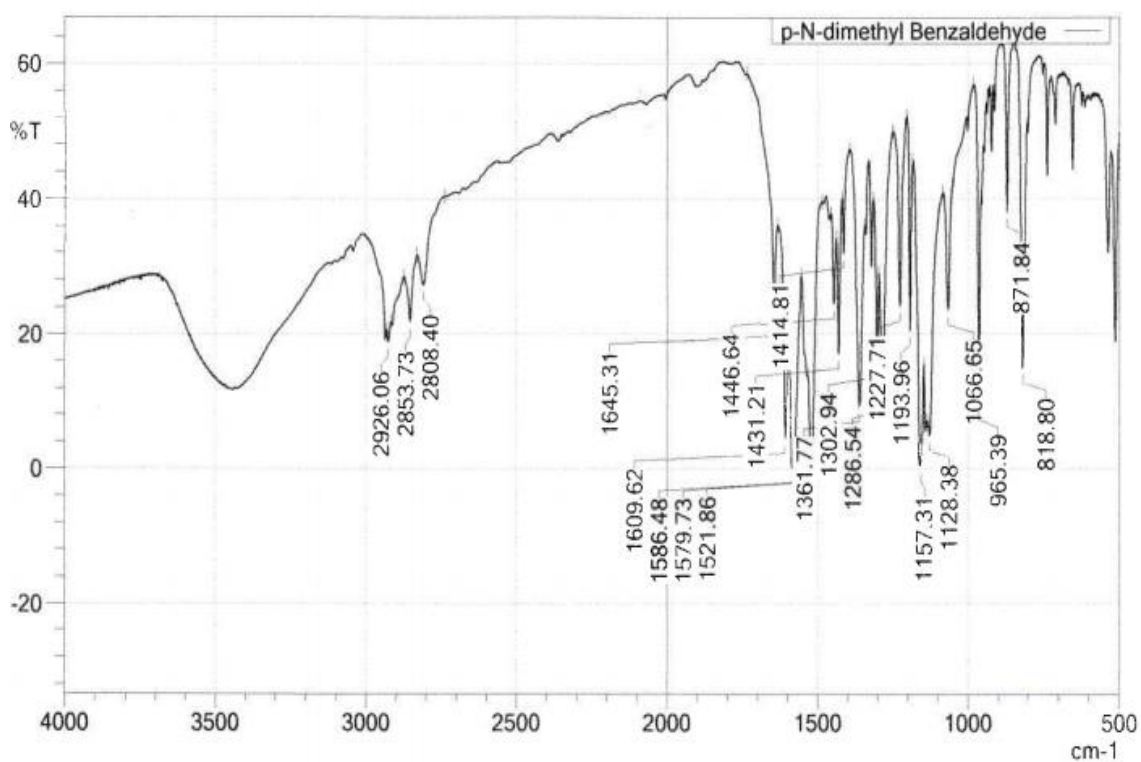


Fig 4.14 IR spectrum of compound 5

 ^1H NMR spectrum

The ^1H NMR spectrum of the compound in DMSO gave the following signals (δ value) using TMS as an internal standard.

^1H NMR (400MHz CDCl_3) $\delta=7.76(\text{s}, 2\text{H}, \text{Allylic}), 7.45(\text{d}, J = 8.8 \text{ Hz}, 4\text{H}, \text{Ar}), 6.71(\text{d}, J = 8.8 \text{ Hz}, 4\text{H}, \text{Ar}), 3.01(\text{s}, 12\text{H}, 2\times\text{N}(\text{CH}_3)_2), 2.94(\text{t}, J = 14.1, 4\text{H}, 2 \times \text{CH}_2), 1.83 -1.79(\text{m}, 2\text{H}, \text{CH}_2)$.

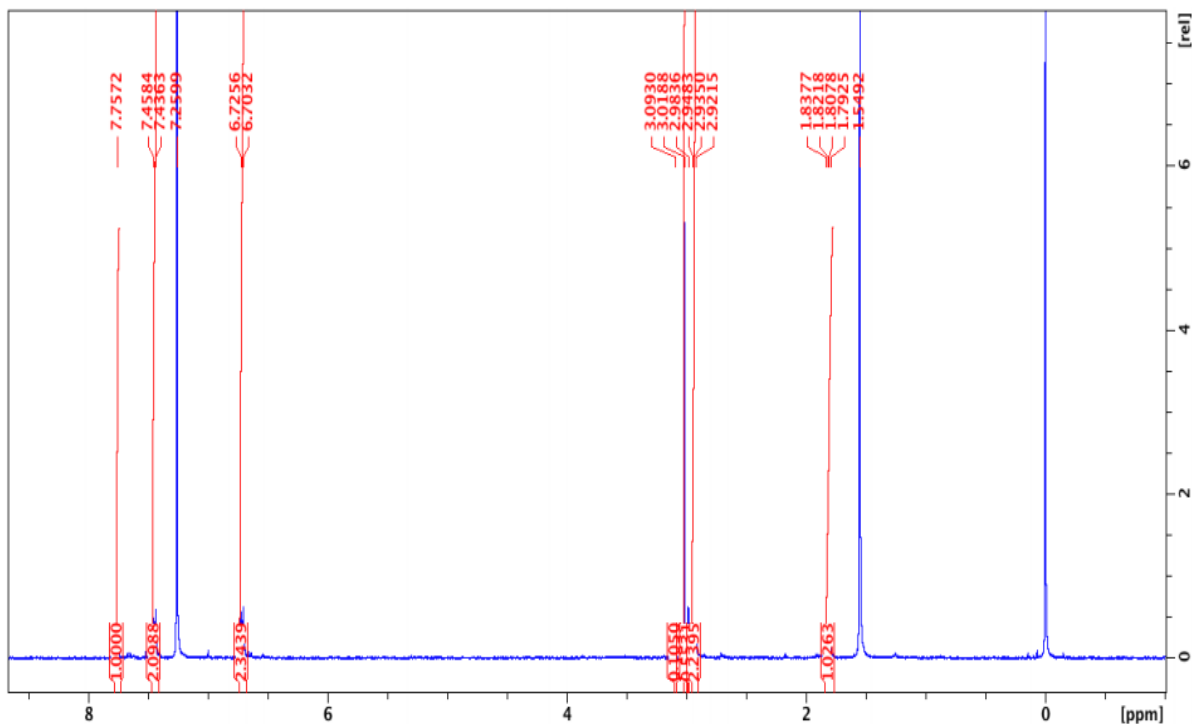
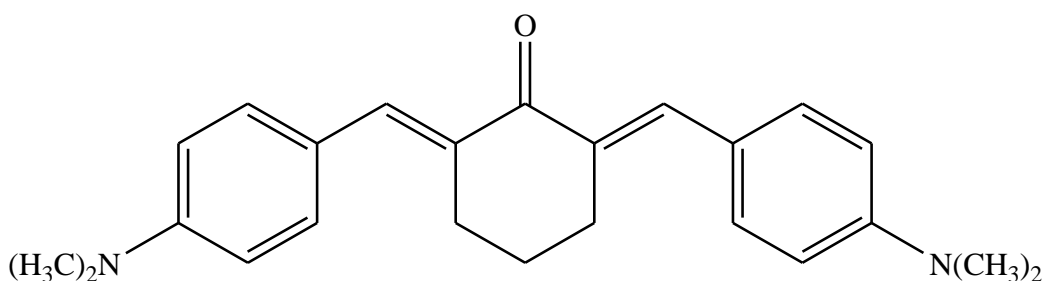


Fig: 4.15 ^1H NMR spectrum of compound **5**

On the basis of the spectral properties (UV, IR & ^1H NMR) and chemical behavior, the following structure has been assigned to the obtained product.

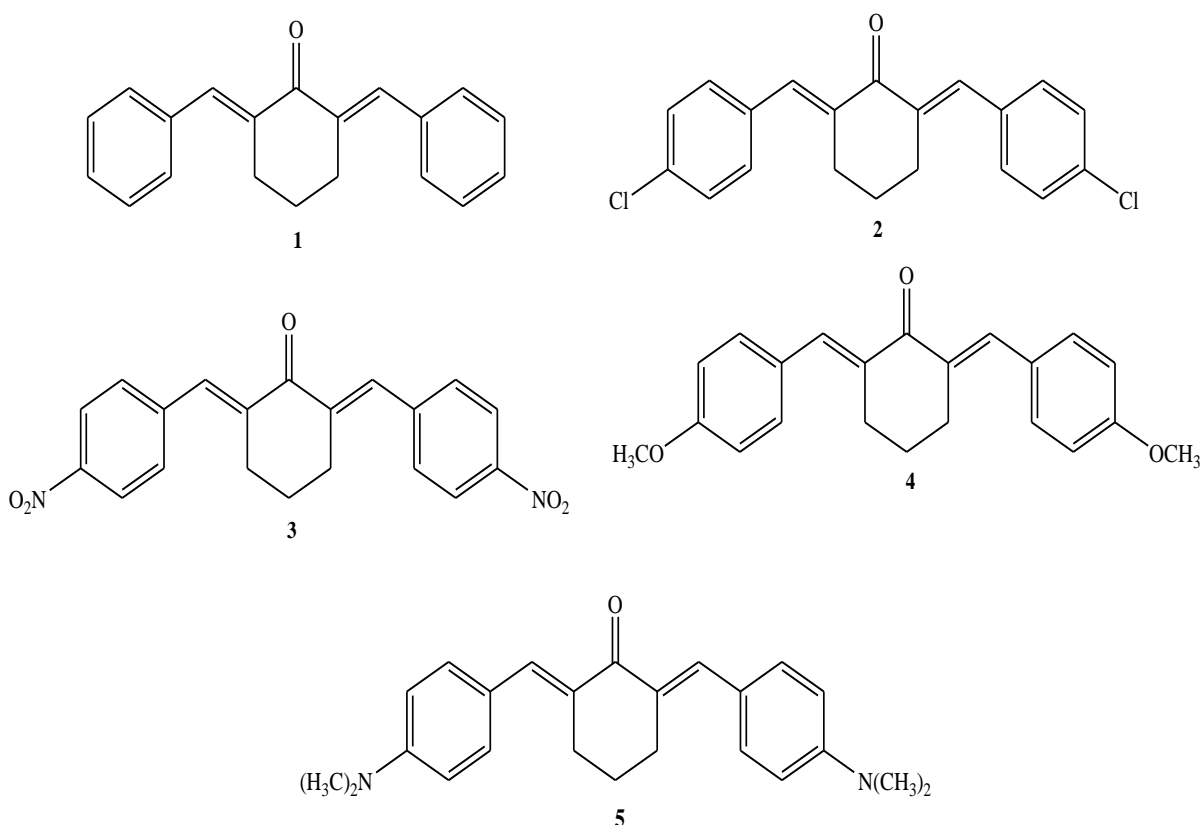


2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone

5

4.6 Photophysical properties

The optical properties of the synthesized bis-chalcone derivatives were studied by UV-Vis spectroscopy. All the compounds were soluble in most organic solvents and exerted absorption above 330 nm. It was observed that 2,6-Dibenzylidene-cyclohexanone **1** absorbed at 330 nm and 2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone **5** showed high absorption at 452 nm.



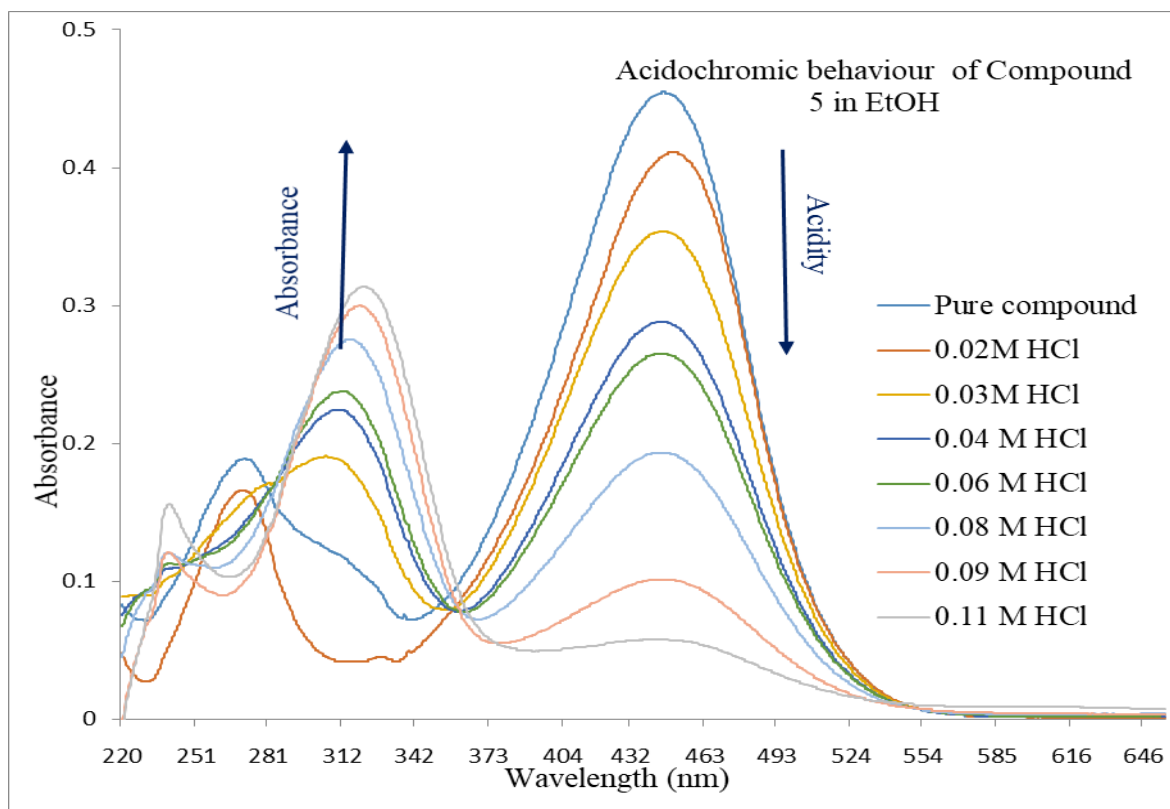
The bathochromic shift for compound **5** is due to the presence of electron donating $N(CH_3)_2$ substituents and the hypsochromic shifts for compound **1** is mainly due to the basic chalcone framework where no substituent is present and hence no substituent effect is noticed. Also 2,6-Bis-(4-methoxy-benzylidene)-cyclohexanone **4** showed absorption at 359 nm (bathochromic shifts, lesser than compound **5**) due to the presence of electron donating methoxy (CH_3O) substituent. Probably the halogen substituent contributed very little effect to the absorption and 2,6-Bis-(4-chloro-benzylidene)-cyclohexanone **2** showed absorption at 333 nm. Further 2,6-Bis-(4-nitro-benzylidene)-cyclohexanone **3** showed absorption at 340 nm.

Table 4.6: Substituent effect

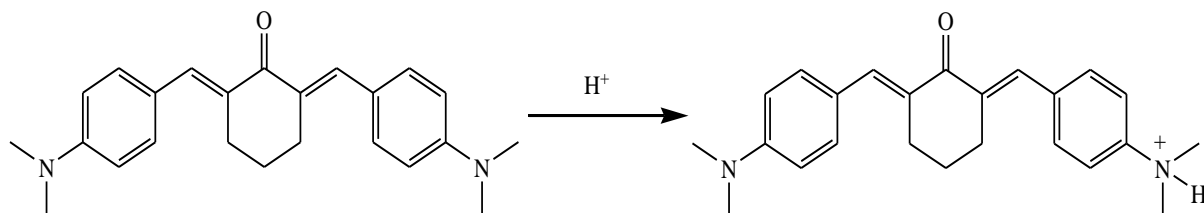
Substituents (R)	λ_{\max} (nm)
H	330
Cl	333
NO ₂	340
MeO	359
N(CH ₃) ₂	452

4.7 Acidochromic behaviour of 2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone **5** in EtOH

The acidochromic properties of 2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone **5** have been investigated. This compound asserted acidochromic behavior with the change in pH. It has shown that the hypochromic shifts ($n \rightarrow \pi^*$) occur with increasing the concentration of acid (HCl) and simultaneously with the lapse of time the absorption maxima becomes sharper and showed a hypsochromic shifts from 452 to 322 nm.

Fig 4.16 Acidochromic behavior of compound **5** in EtOH

This is due to the preferential protonation of chromophoric N,N-dimethyl group, owing to its more basic nature, and resulting in quaternary salt formation. This quaternary system makes the ring strongly deactivated which result in the observed shifts to 322 nm.



On the other hand 2,6-Bis-substituted benzylidene cyclohexanone when treated with HCl it was found no shift in wavelength, though a decrease in absorption maxima was observed. It may be attributed due to decrease in concentration of solution. Similar result was observed for other substituted of bis-chalcone.

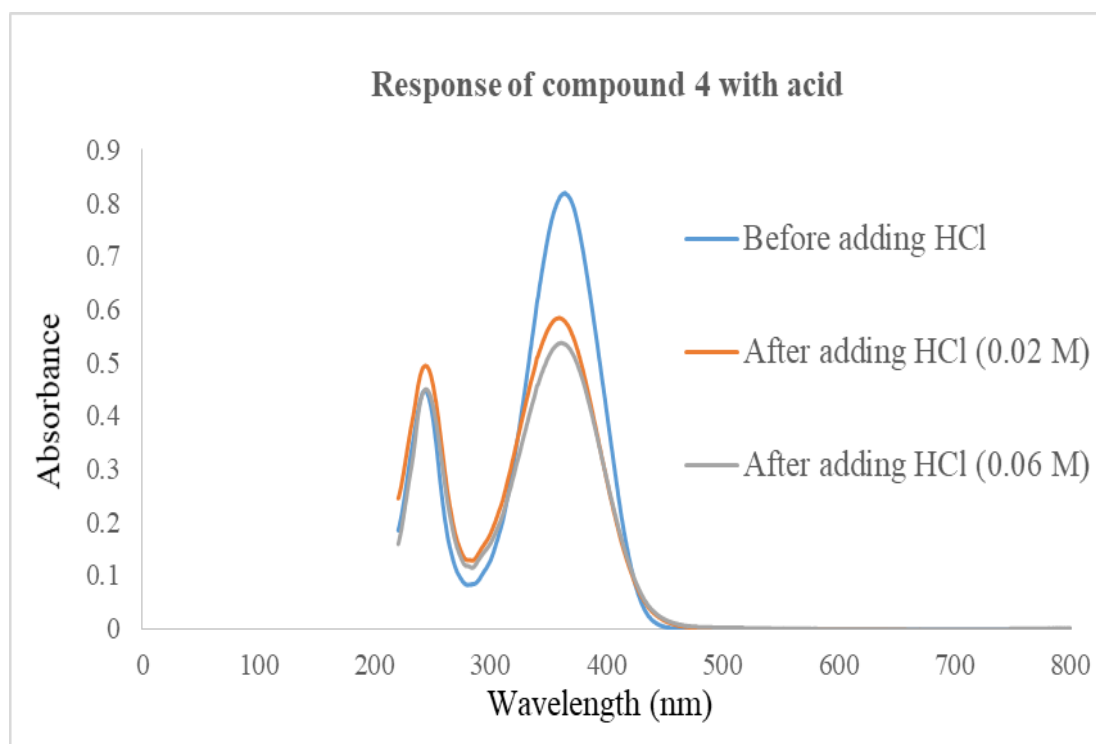


Fig 4.17 Response of compound 4 with acid

4.8 Solvatochromic behavior of substituted 2,6-Dibenzylidene-cyclohexanone

The solute-solvent interactions are different in different kinds of solvents for a given solute. The experimental test results asserted that even if the same solute molecule, the UV absorption energy also changed in different solvents. During studied solvatochromic behavior study of substituted bis chalcone a bathochromic shift in the absorption maxima with the increasing polarity of solvent was observed, excluding compound **2** & **3**. This could be due to the decrease in energy of the excited state as a function of increase in solvent polarity, which is in the order: DCM < Ethyl acetate < EtOH and stabilize the compound.

Table 4.7 Solvent effect

Substituents (R)	DCM (nm)	Ethyl acetate (nm)	EtOH (nm)
H	308	323.5	330
Cl	333	328.5	333
O ₂	340	336	340
MeO	340.5	352	359
N(CH ₃) ₂	358.5	421.5	452

This behavior was accounted as that molecules in the ground state and in the excitation state indicate different polarities. This involved the highly simplifying assumptions that the compounds with non-polarized ground state is more strongly polarized in protic solvents, because the high-energy, polar structure of the excitation state is stabilized. The excited state is lowered, the ground state is hardly affected.

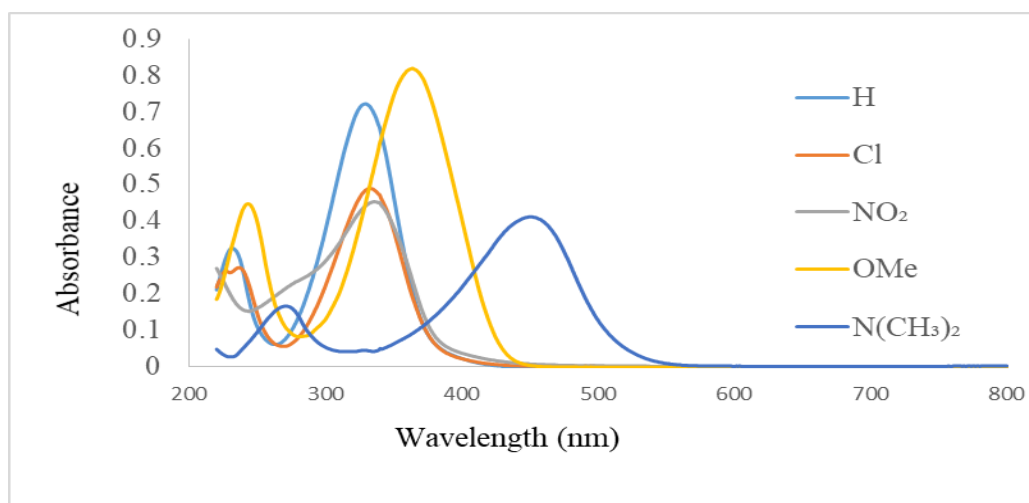


Fig 4.18 UV spectrum of compound **1,2,3,4** & **5** in EtOH

Chapter 5

Conclusion

Chapter 5

Conclusion

This work described the synthesis and characterization of spectral properties of 2,6-Dibenzylidene cyclohexanone based bis chalcone derivatives and the photophysical and optical properties of these compounds have been investigated. First substituted 2,6-Dibenzylidene cyclohexanone was prepared from the reaction between commercially available cyclohexanone and para substituted benzaldehyde in presence of NaOH through the more convenient Claisen-Schmidt condensation reaction of donor-acceptor (D-A) conjugated system. The synthesized compounds were characterized and their structures were elucidated on the basis of UV, IR & ^1H NMR spectra. It was observed that 2,6-Bis-(4-dimethylamino-benzylidene)-cyclohexanone **5** asserted acidochromic behavior with the change in pH. These synthesized compounds contain electron donor-acceptor moieties which exhibited an intramolecular charge transfer (ICT) excited state and hence are found to show solvatochromic behavior. During solvatochromic studies it has also found that the solute-solvent interactions are different in different kind of solvents with increasing the polarity of solvent for a given solute. This could be due to the decrease in energy of the excited state as a function of increase in solvent polarity, which is in the order: DCM < Ethyl acetate < EtOH and stabilize the compound. A significant bathochromic shifts are founds for compounds **1,4** & **5** from increasing order of DCM < Ethyl acetate < EtOH depending on the strength of hydrogen bonds. A positive solvatochromism is observed for the ($n \rightarrow \pi^*$) absorption in EtOH in case of these substituents, whereas a negative solvatochromism is observed ($\pi \rightarrow \pi^*$) for the polar aprotic solvent. These bichromophoric molecules are belong to the group of organic donor acceptor (D-A) compounds and due to this phenomena these compounds are widely used as fluorescence probes for sensing DNA and metal ions.

During solvatochromic behavior study in case of dichloromethane (DCM) compounds **2** & **3** exerted deviation from the basic phenomena of all other compounds most probably due to the unique properties of the substituents Cl & NO_2 group which is our concern and will be further studied.

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