Synthesis of Novel Silica Encapsulated Spiropyran based Thermochromic Materials

ISLAMABAD

A Dissertation submitted to the Department of Chemistry, Quaid-i-Azam University, Islamabad, in partial fulfillment of the requirements for the the degree of

MASTER OF PHILOSOPHY

IN

ORGANIC CHEMISTRY

By

ANILA IQBAL

DEPARTMENT OF CHEMISTRY

QUAID-I-AZAM UNIVERSITY

ISLAMABAD

2012

<u>In the name of ALLAH the most benificient, the most merciful</u>

SAYING OF ALLAH (SWT)

He makes the night grow longer by shortening the day, and makes the day grow longer by shortening the night; and He has full knowledge of what is in the hearts [of men].

(SURAH YASIN)

SAYING OF HOLY PROPHET (PBUH)

"One hour's meditation on the work of the creator is better than seventy years of prayers"

(HADITH)

ALL MY ACHIEVEMENTS ARE DEDICATED

TO

MY DADA G

SIKANDER KHAN QURESHI (late)

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First and foremost all praises and glory be to almighty ALLAH, the only creator of the whole universe, the Most benevolent & most merciful, who created us as a Muslim and blessed us with knowledge to differentiate between right and wrong. Countless salutations upon the Holy Prophet Hazrat Muhammad (P.B.U.H), the source of knowledge and blessings for entire mankind.

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In the end I want to present my unbending thanks to all those hands that prayed for my betterment and serenity.

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ABSTRACT

A series of novel spiropyrans were synthesized through the condensation of substituted 3,3-dimethyl-2-methyleneindoline with differentnitro substituted *o*-hydroxy aromatic aldehydes. Indoles were substituted initially with a variety of alkanes and esters moieties. The substituted 3,3-dimethyl-2-methyleneindoline were reacted with nitro substituted *o*-hydroxy aromatic aldehydes to yield the respective spiropyrans. The synthesized novel spiropyrans were encapsulated in silica nano-shells to protect them from the effect of moisture and p^H. The thermochromicbehavior of novel spiropyrans was studied by UV-Visible spectroscopy. The thermally induced isomerizationof spiropyrans derivatives was carried out in water/ethanol mixture. The thermal isomerization of SP (colorless form) to MC (colored form) was discontinuous process as observed through a temperature change of 5-60 °C with the UV-Visible spectrometer. The absorption process occurs reversibly regardless of the heating /cooling sequence. The spiropyran derivatives therefore have a potential application for colorimetric temperature indication.

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STANDARD ABBREVIATIONS

b	Broad
bs	Broad signal
$^{\circ}C$	Degree Celcius
cm^{-1}	Wave Number
d	Doublet
dd	Doublet of doublet
Hz	Hertz
J	Coupling constant (in NMR spectroscopy)
m	Multiplet
m.p	Melting point
NMR	Nuclear magnetic resonance
ppm	Parts per million
R_f	Retension factor
s	Singlet
t	Triplet
TLC	Thin layer chromatography

Chapter 1
INTRODUCTION

Materials science is a very broad interdisciplinary field that spans many areas of scientific research, with recent exciting developments arising from our increasing ability to control the behavior of bulk materials through manipulation at the molecular level. The key to large-scale development of chem/bio-sensors lies in fundamentals of materials Science.

Color changes provide an important signal that can be used to communicate information about the surrounding environment in a fast and effective way. Furthermore, when the color variation is fully reversible, the possible applications widens significantly, especially in terms of sensors and biosensors.

Conventional chemical and biological sensors depend on selective reactions at active surfaces which are directly exposed to the sample. These active surfaces generally tend to change over time and processes like fouling, decomposition or leaching, significantly influence the efficiency of chemo/bio-sensor. Operating characteristics (sensitivity, selectivity and baseline) and consequently devices must be calibrated or in other words, the sensing surface should periodically be removed from the sample and re-characterized. Therefore, accurate in-situ chemical monitoring typically requires relatively complex instrumentation that incorporates pumps, fluidic manifolds, detectors, reagent reservoirs and highly skilled operators.

Ultimately the possibility of an adaptive material, whose sensing surface, after the sensing process has been performed, can be then restored exploiting the reversibility of the conversion at a molecular level, can lead to a completely different approach to chemical sensing. In principle these devices may be capable of addressing the so called “chemical sensing paradox” of combining the absolute requirement of an active surface to bind the target species, with passive behavior that minimizes changes in the surface binding characteristics over time, in order to reduce the need for calibration.

1.1Temperature Sensors

A precise and accurate measurement/monitoring of temperature is an important part of scientific research/development and industrial processes control because temperature effects the physical/chemical properties of almost allmaterials. Many

techniques have been developed to sense/monitortemperature for different applications for example the volumetric expansion of liquid mercury or an organic liquid in a small capillary has been used for long time to measure the temperature. The linear expansion of silica optical fiber has been used in designing the Bragg-gratting based optical fiber temperature sensors. The electrical resistance of metals and the semiconductor is temperature dependent and temperature sensors have been designed based on measuring the resistance or conductivity of metals or semiconductor materials. Thermocouples are another class of temperature sensors based on the measurement of optical properties. A thermocouple is based on the measurement of voltage drop across the dissimilar materials which are temperature dependent. Temperature also affects the resonance frequency of the piezoelectric crystal and temperature sensors based on this phenomenon have been reported.

Several optical techniques have been used to measure /monitor temperature. Plank's model of black body emission forms the basis of temperature measurements through monitoring infra-red emission from a target sample. Optical emission from free radicals, atoms or ions in high temperature gas or plasma have been used to remote monitor temperature of high temperature furnace, or combustion system and rocket tail plume. Fluorescence quenching is an optical spectroscopic technology used to sense temperature. The thermochromic response of an organic dye encapsulated in a polymer and thermochromic polymers have alsobeen used to sense temperature. The optical absorption of these thermochromic materials changes with the change of temperature, which gives the sensing signals[1].

1.2 Chemichromism

Chemichromism is a termreferring to a general color change, induced by an external stimulus (chemical or physical)[2]. Many classes of compounds undergo color changes due to heat, light, electrical current, pH changes or the presence of metal ions.

The color change phenomena can be classified according to the different causes which determine them. Some examples are: solvatochromism, photochromism, thermochromism, electrochromism, ionochromism and halochromism where the stimulus

is respectively: light irradiation, heat, electrical current, solvent polarity, presence of ions and pH changes[3].

1.2.1 Photochromism

"Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra" (**Figure 1.1**).

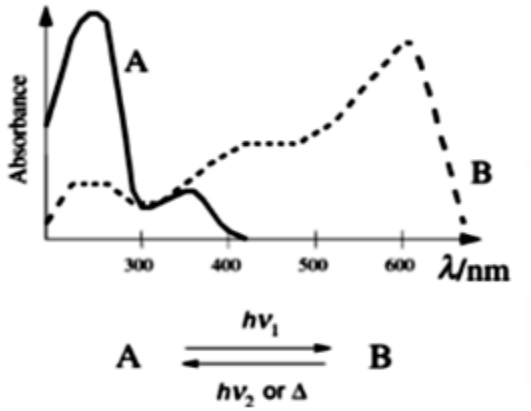


Figure.1.1:Reversible transformation of chemical species

The thermodynamically stable form A is transformed by irradiation into form B. The reverse reaction can occur thermally or photochemically. The most prevalent organic photochromic systems involve unimolecularreactions: the most common photochromic molecules have a colorless or pale yellow form A and a colored form B (e.g., red or blue). This phenomenon is referred to as positive photochromism[4].

1.2.2 Solvatochromic

The solvatochromic effect occurs where there is a strong dependence of the UV-Vis absorption bands of a compound on variations in the polarity of the solvent medium. It involves a change in the position and sometimes in the intensity of the absorption bands of the molecule when measured in different solvents. These changes are caused by intermolecular interactions between the solute and solvent that modify the energy gap between the ground and excited state of the absorbing species[5]. Consequently, variations

in the position, intensity and shape of the absorption spectra can be a direct measurement of the specific interactions between the solute and solvent molecules.

The family of spiropyran compounds undergoes solvatochromism, as the equilibrium between the ring closed spiro (SP) form and the ring open merocyanine (MC) form is influenced by the external medium in which the molecule is dissolved[6].

The solvatochromism of spiropyrans depends on three main factors:

1) Solvent polarity.

2) Nature of the substituent groups.

3) Concentration of the solution.

1.2.3 Electrochromism

The reversible change of absorption spectra between two forms, A and B, resulting from electrochemical (oxidation/reduction) reactions is termed as electrochromism[7].

1.2.4 Ionochromism

Ionochromism is the reversible change of absorption spectra between two forms A and B, resulting by the presence of ions.

1.2.5 Halochromism

When the absorption spectra between two forms, A and B is changed reversibly due to the change in the pH. Its termed as Halochromism[8].

1.3Thermochromism

One of the definitions of thermochromism says that it is a reversible color change observed for a variety of compounds with temperature variation[9]. A more precise definition has been given by Day, “Thermochromism is defined operationally as an easily noticeable reversible color change in the temperature range limited by the boiling point of each liquid, the boiling point of the solvent in the case of solution or the melting point for solids.”[10].

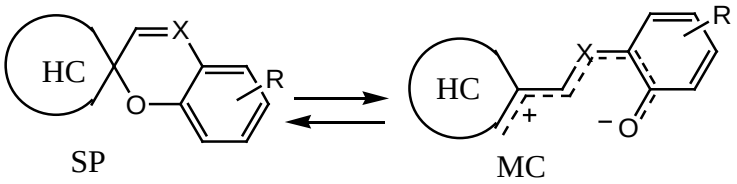
In the current study theorganic compounds for which the observed reversible color changes (coloring and fading reactions) are due to the effect of temperature are discussed. Exclusively from many organic photochromic compounds (e.gspiropyrans, anils,and hydrazones)for which the color change is photochemically induced, the bleaching reaction is at least partly thermally controlled.

Color change induced by thermochromic behavior occurs when certain temperature of thermochromic transition is reached. This transition temperature varies for different thermochromic compounds. Color change is usually slow process; hence it can appear to occur in some temperature range.

1.4ThermochromicSpiroHeterocyclic and Related Compounds

The thermochromism of spiropyrans has been extensively studied. Nearly every known compound of this class leads to deep color on melting (generally red, purple, or blue). However, heating solutions of spiropyrans also causes coloration. Day[9] in his review reported essentially thermochromicspiropyrans of the indoline and spirobipyran series. Bertelson[11] summarized the main spectroscopic and physicochemical data obtained up to 1971. Thermochromic properties of spirooxazines have been reported more recently[12].

Spiropyrans and spirooxazines are known in particular for their photochromic behavior, but they also exhibit thermochromic behavior. The thermochromism of spiropyrans was discovered in 1926 and since that time it was extensively studied[9].The thermochromic mechanism in these classes has been assumed to involve a thermally sensitive equilibrium between the colorless spiroheterocyclic form (SP) and the quasi-planar open merocyanine-like structure (MC) obtained after the breaking of the C–O bond (**Scheme 1.1**).

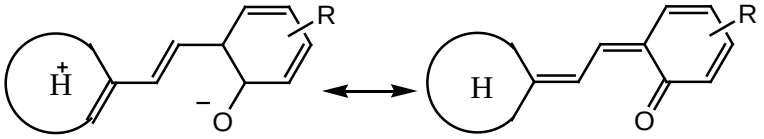


HC = heterocycle; R = alkyl residue

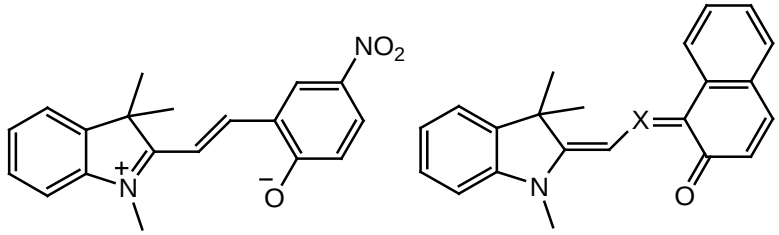
X = CH (spiropyran) X = N (spirooxazine)

Scheme 1.1:Resonance between spiroheterocyclic form and open merocyaninelike structure of spiropyran and spirooxazine

For both these classes of spiroheterocyclic compounds, it seems certain that the thermally most stable photoinduced colored form and the species formed thermally are spectroscopically and kinetically indistinguishable. Depending on the structure, different isomers of the colored form can be involved, but the most stable corresponds to an *E* configuration[11, 13-17]. The electronic distribution of the open form is situated between two resonance forms, its proximity to one form or the other depends on the structure and the medium (**Scheme 1.2**). For example, spiro[indoline-pyrans] bearing a 6-NO_2 group would be zwitterionic, whereas spiro[indoline-naphthopyrans] or spiro[indoline-naphthoxazines] would be quinoidal[16-23] (**Scheme 1.3**).



Scheme 1.2: Resonance forms, general equation.

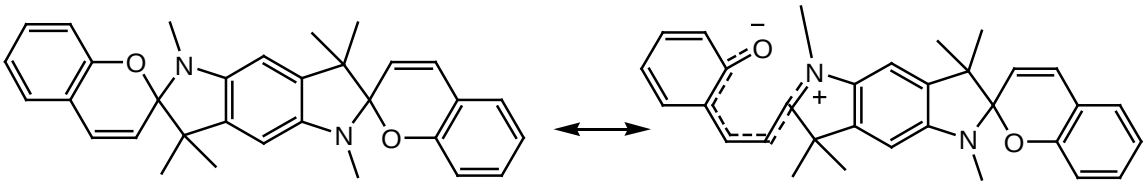


X=CH (Spiropyrans)

X=N (Spirooxazines)

Scheme 1.3: Resonance forms of spiropyrans and spirooxazines

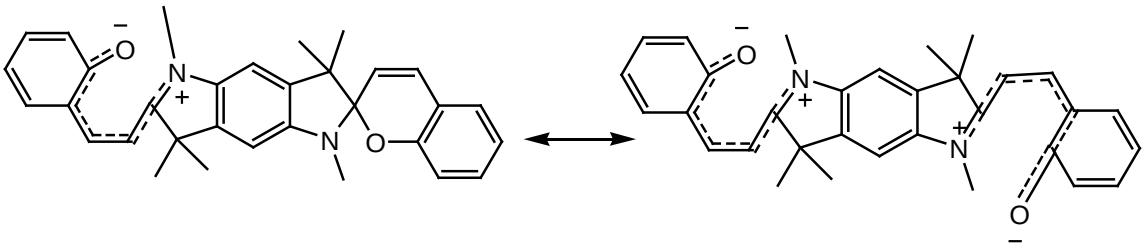
There are many different spiropyran groups possessing thermochromic behavior. For example, spiropyrans of the 2-oxaindane or azaindanone series with polycondensed chromene fragment have been synthesized as well as dithiolane series by Russian teams. Bridged spiropyrans are another group, colorless, in the spiroheterocyclic form and their heating from 40°C to 80°C causes reversible coloration to blue color. Besides monospiropyrans, also bis-spiropyrans have been extensively studied. These substances consist of two pyran rings separated by a group of atoms with saturated bonds.Coloration of bis-spiropyrans is usually sequence coloration. In the first phase (heating within certain temperature range) only onepyran ring (chromophore) opens (**Scheme 1.4**).



SP-SPMC-SP

Scheme 1.4: Transformation between spiroheterocyclic–spiroheterocyclicstructure and merocyanine-spiroheterocycliclike structure

During the second phase (heating to the temperature above the temperature range), remainingchromophore opens (**Scheme 1.5**)

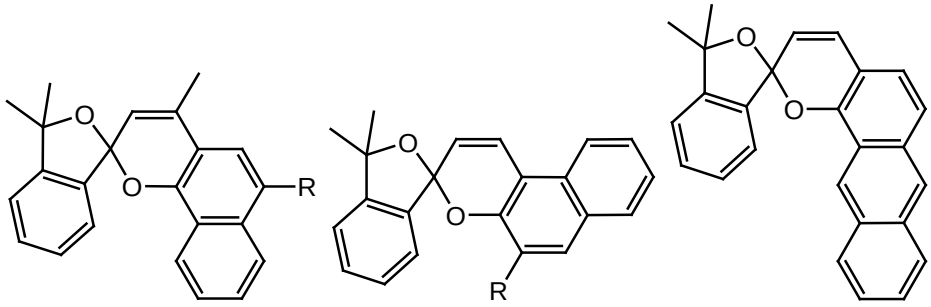


MC-SPMC-MC

Scheme 1.5: Transformation between spiroheterocyclicspiroheterocyclic structure and merocyanine like – merocyaninelike structure

Newthermochromicspiropyrans have been synthesizedby Minkin and co-workers[24, 25]. For example, spiropyrans of the 2-oxaindane or azaindanone series with

polycondensedchromene fragments (**1–8**) (**Figure 1.2**) exhibiting photo and thermochromicproperties.



1: R=H,**2**: R=Br, **3**:R=NO_2**4**: R=H, **5**: R=OH**6**

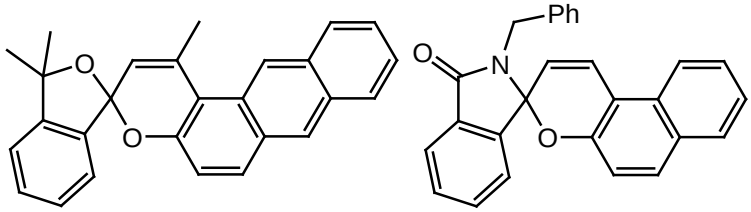


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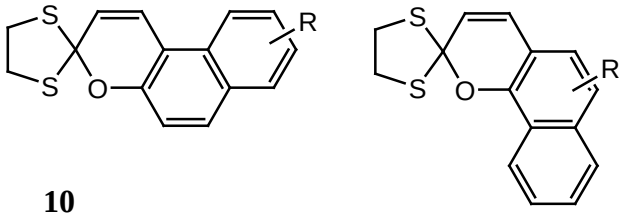
Figure 1.2:Spiropyrans of the 2-Oxaindane or Azaindanone series

Krasieva and co-workers[26] mentioned the thermochromic behavior of spiropyrans of the dithiolane series (**9, 10**) (**Figure 1.3**). These data confirm that the annellation of the benzopyran moiety favors the thermochromic properties of this class of compounds.



9 **10**

Figure 1.3: Spiropyrans of the Dithiolane Series

An important contribution from Hellrung and Balli[27] concerned the thermochromism of a series of spiropyrans**(11–20)**(**Figure 1.4**)in various solvents such as benzyl alcohol, dimethyl phthalate, decalin, toluene and xylene.

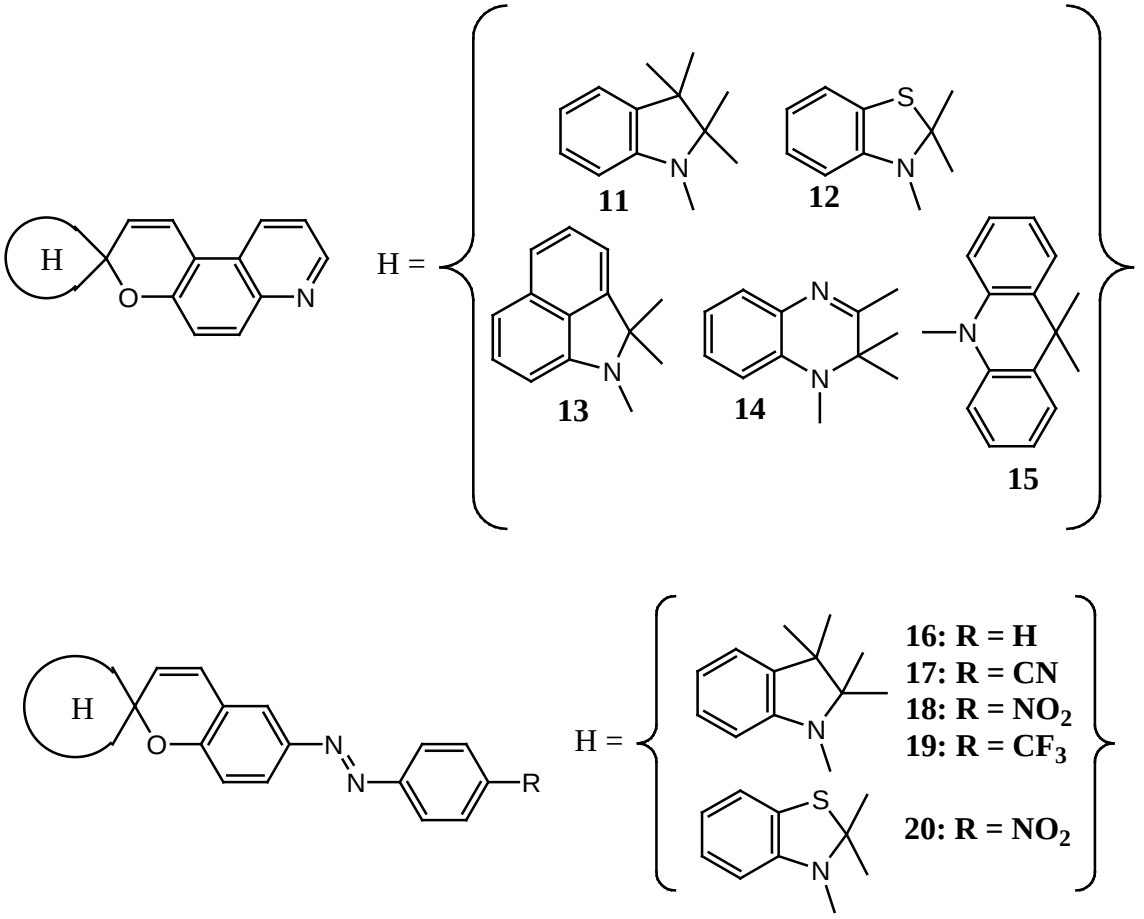


Figure 1.4: Series of Spiropyrans showing solvent dependence.

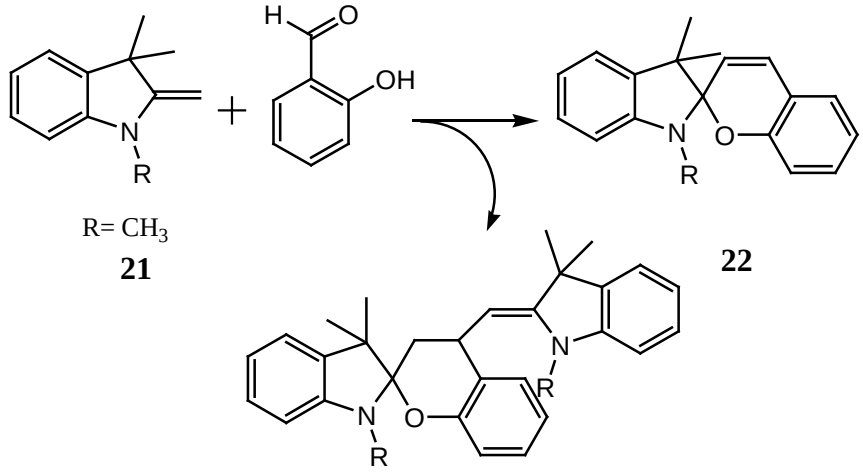
1.5Synthesis of Spiropyrans

The standard methods for the synthesis of spiropyrans remain practically unchanged and can be divided into two main groups.

1) Condensation of methylene bases (or their precursors) with *o*-hydroxy aromatic aldehydes.
2) Condensation of *o*-hydroxy aromatic aldehydes with the salts of heterocyclic cations containing active methylene groups, isolation of the intermediate styryl salts, and subsequent removal of the elements of the acid[28].

1.5.1 Production of spiropyrans by condensation of methylene bases with *o*-hydroxy aromatic aldehydes

This method is characteristic of the synthesis of spiropyrans of the indoline series **22**, the method for the preparation of which remains practically unchanged from the time of Wizinger's work[29]i.e., boiling the methylene bases of nitrogen heterocycles (for spiropyrans of the indoline series the Fischer base **21**)and *o*-hydroxy aromatic aldehydes in suitable solvents (most often in alcohol). In some cases it is convenient toconduct the reaction in DMF. In the proposed form, however, this reaction often leads to side products (**Scheme 1.6**) of the type **23**[30].

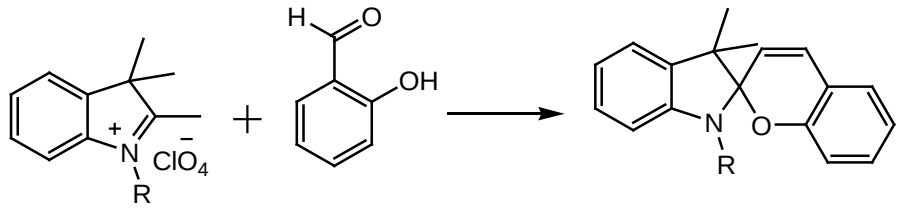


21 **22**

23

Scheme 1.6: Production of spiropyrans by condensation

In order to reduce the yield of the "dicondensed" side product it is recommended to use the corresponding quaternary indolenylium salt **24** in a mixture with an equimolar amount of an organic base (most often piperidine) instead of the methylene base (**Scheme 1.7**).



24

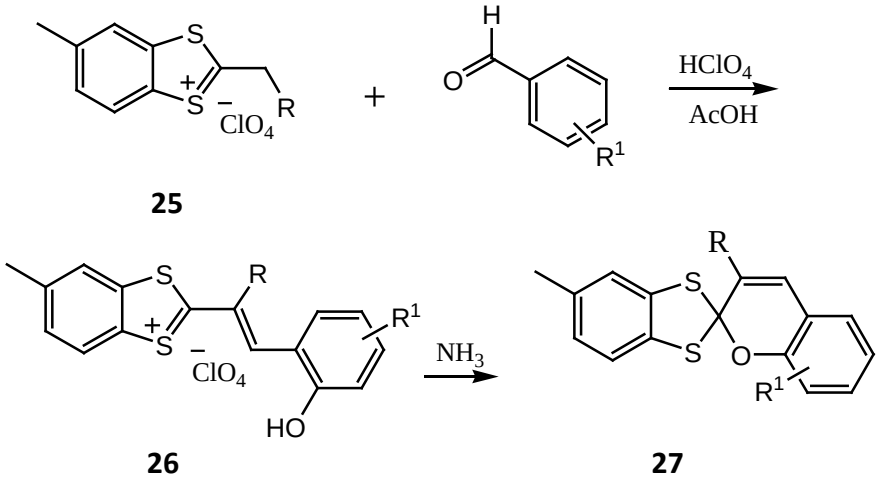
Scheme 1.7: Production of spiropyranfrom corresponding quaternary indolenylium salt

Spiropyrans are most commonly synthesized by this method using alcohol as solvent and the product is obtained by filtration[31].

1.5.2 Production of spiropyrans by condensation of *o*-hydroxy aromatic aldehydes with salts of heterocyclic cations

The standard procedure in this case is condensation of *o*-hydroxy aromatic aldehydes with the salts of heterocyclic cations followed by removal of the elements of the acid from the obtained styryl salt with organic bases (gaseous ammonia or amines).

Spiropyrans of general type **27**were synthesized in a similar way by the condensation of 2,5-dimethyl- and 2-ethyl-5-methylbenzo-1,3-dithiolium perchlorates **25**with substituted aromatic *o*-hydroxybenz(naphth) aldehydes with heating for 5-10 min in acetic acid at 90-100°C with a catalytic amount of perchloric acid (with isolation of the styryl salt **26**)[32]. The styryl derivatives **26**, obtained with yields of 60-80%, are deeply colored crystalline substances. The elimination of the elements of perchloric acid from them, leading to the spiropyrans**27**, is achieved with the highest yields by treatment of the derivatives **26**with an ether or benzene solution of dry ammonia (**Scheme 1.6**).



Scheme1.8: Production of spiropyrans by condensation of *o*-hydroxy aromatic aldehydes with salts of heterocyclic cations

1.6Structural Features

Anumber of generalizations can be made about the structural requirements for thermochromism of spiropyran:

(1)The pyran ring must be at least a naphthopyran. Benzopyrans are not usually thermochromic, but they may be, depending on the specific nature of the heterocyclic ring, such asindolinobenzospiropyrans have the thermochromic properties.

(2) Substitution on the 3'-carbon prevents thermochromism by making the required planar, open form sterically impossible. The weak thermochromism of 3,3'-dimethylene and 3,3'-trimethylenedi-6-naphthospiropyran confirms rather than refusing the idea, since they do not prevent the required planarity whereas the puckered ring of the 3,3'-tetramethylene compound does, and it is not thermochromic. Other 3'-substituted thermochromic compounds are known, particularly the isospiropyrans.

(3) The extent to which a compound is thermochromic is related to the electron releasing ability of the heterocyclicring.

(4) Substitution on either ring enhances thermochromism if it contributes to the positiveness of the spiro carbon or the heteroatom or to the negative charge on the oxygen of pyran ring[9].

The compounds which exhibited excellent photochemical and thermal colorability, can be suitably tuned upon changing applications[33].

An *o*-hydroxyphenylcontaining spiropyranthermochromic colorant was synthesized. The prepared compound was sensitive to temperature and has a reversible color change with temperature variation. Thethermochromism of the compound presumably involved a ring-opening C-O bond cleavage of the spiropyran moiety followed by an intramolecular hydrogen transfer[34].

However, in the last decades, the application of spiropyran in optical memory and optical switches has been hindered by the short half life time of the colored MC form, which reverts thermally to the ring closed colorless spiropyran. Various methods to stabilize the MC form have been developed.

A monolayer ofspiroxazine dye was deposited on a gold surface that involved the covalent linkage of the dye to a cystamine monolayer modified gold. The self-assembly process on gold is initiated by strong interactions between the hetero atom head-group and the gold surface which are believed to result in chemisorption of the molecules, which forces them to become commensurate with the gold lattice[35].

The photochromic property of spiropyran dye could be controlled by the change of molecular structure surrounding the dye in the guest host system. The intermolecular cycloaddition between chalcone units in polymerscan reduce the excluded volume surrounding spiropyranand merocyanine molecule, which lowersthe rate of photochromic process, significantly,compared to that in a photochemically inertmedium.

The rate of decolorization process of spiropyran can be controlled with various ways e.g changing the molecular environment of photochromic moiety. When the spiropyran moiety changes their chemical structure (ring opening and *cis–trans* isomerization) to merocynine chromophore, a certain extent of free volume is necessary to change their molecular structure and shape. The photocrosslink of chalcone moiety can induce steric hindrance during the photochromism and it can also effectively retard the rate of photochromic decolorization. It was proved that the photocycloaddition of the chalcone groups in main chain polymer affects the decolorization of photochromic dye effectively than that in side chain polymer[36].

Strong inhibition of the backward reaction isdemonstrated in spiropyrans when a cationic moiety is attached to the *ortho*position (8H)to phenolate ion. The ionic substituent effect is three times more effective than the known solvent effect and provides an active method of tuning and designing new chromic molecules.The incorporation of an ionic moiety in the molecular skeleton of spiropyran, reverse ring closure by suppression or acceleration becomes possible. The ionic moiety has both an electronic (modification of HOMO–LUMO energies)and Coulombic(charge interaction between phenolate and indoline)influence on the merocyanine. Although it is not possible to elucidate which factor governs the reaction. Since, both modify the rate in the same direction[37].

A simple method to improvethe thermal stability of the open-ring merocyanine (MC) form could be realized by decreasing the electron density of the oxygen atom via

introducing electron-withdrawing groups or hetero atoms to the naphthalene ring. The use of a fluorescent intermediate of 3-amino-4-hydroxy-1,8-naphthalimide as the spironaphthoxazines framework. The naphthalimide unit is incorporated at the naphthoxazinefragment, thus giving a strong electron-withdrawing effect favoring the long-lived MC in the dark and giving good colorability in solution. A significant stabilization of the photomerocyaninewas observed. Remarkably, their open MC forms are stable with long lifetimes. Moreover, the fluorescence of naphthalimide unit can be switched on and off by photoinduced conversion[38].

Addition of metal ions (such as Mg^{2+}, Ca^{2+}, Eu^{3+}) decreases the first-order thermal decoloration rate constants to different extent. The colored forms of the compound are more stable than the parent spirobenzopyran. It provides a method of increasing stability of the merocyanine forms which are of high importance for applications of thermochromic/photochromic materials,especially in the presence of Eu^{3+}. The compound may be applied as thermochromic/photochromic materials for its high thermal stability of colored forms[39].

Incorporation of a crown ether moiety to the spiropyran skeleton offers a great variety of properties, including the control of the photo/thermoisomerization of the spiropyran ring by complexing alkali cations. Crowned spirobenzopyrans were also attached to polymers and membranes. The purpose was to combine the unique properties of the calix [4]-arene ring, the crown ether ring and the spiropyranskeleton. The kinetics of thermal decay of the merocyanine form of the calixcrownspiropyran molecule shows a biexponential character in both solvents, while the decay is much slower in ethanol than in acetonitrile[40].

1.7 Encapsulation of Spiropyrans

The covalent binding of spiropyrans into polymeric matrices can significantly reduce their photodegradation that is an important limitation to practical application[41].

Sol-gel glasses have attracted much attention in recent times as encapsulation matrices for molecular entities. These materials have been used in many applications related to the development of different sensors through encapsulation of response active molecules[42].

A significant retardation of the decay rate was observed for spiropyrans substituted with a succinyl ester functionality in a gel. The gel network has been shown to consist of a three dimensional network and it is hypothesized that a unique mode of interaction exists between the succinyl group of the spiropyran and the gelling agent. The lifetime of the colored merocyanine was increased by over 300-fold in the organogel versus solution with a succinyl ester functionality present. Structurally similar spiropyrans without the succinyl ester functionality showed relatively little change in the lifetime of the merocyanine[43].

Spiroxazine group showed reversible isomerization in substituted methacrylamide polymer upon irradiation. The resulting polymer was found to be thermochromic/photochromic in solution and in thin solid film[44].

Reversible and stablethermochromic/photochromic properties were attained by incorporation of spiropyran and organic acid between the interlayers of layered compounds. An important situation of the systems was the presence of hydrophobic and hydrophilic regions because SP is stable in hydrophobic regions and the MC form is stable in the hydrophilic region. The organic anions were incorporated among silica matrix homogeneously by the sol-gel method. Spiropyran incorporated in the silica matrix exhibited photochromic properties in the presence of organic sulfonic acid. For acids having a benzene ring and a long alkyl group, high reversible and stable thermochromic/photochromicproperties were attained[45].

Reversible and stable photochromic properties of sulfonatedspiropyran ($SP\text{-}SO_3^-$) were achieved by trapping $SP\text{-}SO_3^-$in a silica matrix by the sol-gel route. The presence of organic anions was essential for the photochromic properties, indicating the importance of the coexistence of polar and non-polar regions. Thin films of silica matrix containing $SP\text{-}SO_3^-$, various acids were added to form non-polar regions within the silica matrix. $SP\text{-}SO_3^-$ and organic acid were mixed without a silica matrix, and the photochromic properties were measured although a clear transparent film was not obtained. In the presence of acid, reversible photochromic properties were obtained even without a silica matrix. However the thermal stability of $MC\text{-}SO_3^-$ was less than that in the silica matrix. The necessity of a silica matrix and an organic acid indicate the important role of the silica matrix in distributing $SP\text{-}SO_3^-$ and acid well.

The reversibility of SP-SO_3^- trapped in a silica matrix depends on the kind of sulfonic acid used. In a sol-gel process, it is easy to control the composition of nanocomposites, and so the coexistence of neutral compounds with SP is possible.

Especially,in the case of(perhydrosilazane) PSz/m-xylene solution,because PSz converts into colorless transparent silica film under the ambient condition[46].

Spiropyran derivatives having octadecyl group, hydroxyl group (SPOH) and carboxyl group (SPCOOH) were dispersed into various matrices such as chloroform solvent, polymethylmetacrylate (PMMA)/acetone solution and poly (PSz)/m-xylene solution. Thermal stability of photomerocyanine isomer (PMC-form) in spiropyran derivatives dispersed in silica composite film showed that the Intensity at λ_{max} of PMC-form in silica composite film keeps at initial values in long time except for one having octadecyl group. PMC-form of SPOH and SPCOOH forms intermolecular hydrogen bonding between hydroxyl or carboxyl group and oxygen atom in silica matrix. Therefore, PMC-form of SPOH and SPCOOH in silica composite film is stabilized dramatically[47].

1.8 Applications of Thermochromic Compounds

1.8.1 Inks

In 1970s thermochromic inks or dyes were developed, that temporarily change color with exposure to heat. There applications include flat thermometers, battery testers, clothing, and the indicator on bottles of syrup that change color when the syrup is warm. The thermometers are often used on the exterior of aquariumsor to obtain a body temperature via the forehead. Some of the companies use thermochromicink on their products cans, change of color indicatesthat the can is cold.

1.8.2 Paints

Thermochromic paint is a relatively recent development in the area of color-changing pigments. Thermochromic paints are seen quite often as a coating on coffee mugs, whereby once hot coffee is poured into the mugs, the thermochromic paint absorbs the heat and becomes colored or transparent, therefore changing the appearance of the mug.

1.8.3 Papers

Thermochromic papers are used for thermal printers. One example is the paper impregnated with the solid mixture of a dye with octadecylphosphonic acid. This mixture is stable in solid phase; however, when the octadecylphosphonic acid is melted, the dye undergoes chemical reaction in the liquid phase, and assumes the protonated colored form. This state is then conserved when the matrix solidifies again, if the cooling process is fast enough. As the leuco form is more stable in lower temperatures and solid phase, the records on thermochromic papers slowly fade out over years this may lead to interesting effects in combination with accounting records, receipts from a thermal printer and a tax audit.

1.8.4 Polymers

Thermochromism can appear in thermoplastics, duroplastics, gels or any kind of coatings. The polymer itself is an embedded thermochromic additive. The application of thermochromic polymers for adaptive solar protection is of great interest in the last decade[48].

1.8.5 Optical lock-in Detection (OLID)

Optical lock-in detection (OLID) microscopy is use for high-contrast imaging of a specific class of optically switchable fluorescent probe. Optical switch probes undergo rapid and reversible, optically-drive transitions between two distinct states that differ in their structural, physical, and spectroscopic properties.An example is thespironaphthoxazine (NISO). This provides rational design of optical switch for both fluorescence emission and optical switching. This property is achieved by incorporating tetramethylrhodamine (TMR), a highly fluorescent probe for fluorescent imaging and NISO, a highly efficient optical switchin the same molecule[49].

1.8.6 Other Applications

Thermochromic compoundsare used as color indicators on batteries. The indicator turns green if the battery still possesses a charge. This works by passing the charge of the battery through a small resistor on the battery and causes the pigment to absorb heat. Once the paint has absorbed enough heat from the current of the battery, it changes from black to green (usually), thus indicating that the battery still has a fair amount of charge left in it. Another approach is using a resistor in the shape of a thin triangular layer, under a thermochromic pigment. The variable width of the resistor causes it to be heated unevenly with the position of transition threshold temperature varying depending on the current the battery is providing.

1.9Applications of Spiropyrans

The conceptual aspects of the practical application of spiropyrans in various regions of technology, connected primarily with the thermo-, photo-, solvato-, and electrochromic characteristics[50] were formulated in the monograph[51] and the text book[52] and were supplemented by the review[53].

Spiropyrans of the traditional indoline[54]which are characterized by a shift of the absorption band of the photoinduced form toward the red region of the spectrum[55-57]have found application. Polyester resins have traditionally been used to produce film forms of photochromic materials based on spiropyrans[58, 59]. Photochromic materials from spirancontaining polymeric films deposited on a paper base have become widespread[54, 59]. Synthetic resins with a high refractive index were used to make photochromic lenses[60]. Spiropyrans have even found their uses in cosmetic compositions[61].

The creation of modern photochromic materials[62, 63]requires a combination of new types of spiropyrans[64]with modified supports and in particular Langmuir–Blodgett films containing spiropyran as photoreceptors[65] and also films containing rhodopsin to increase the level of the photosignal[66].

Photochromic materials based on spiropyrans sensitive to UV radiation[67]have traditionally been used as detectors[68] for the protection of sight organs[69] for the creation of light filters with modulated transmission and devices based on them[70] and photochromic lenses[71] including ophthalmic lenses[72].

The use of compositions based on spiropyrans for the creation of materials for recording optical data[73, 74]in various devices[75] including thin films[76] was supplemented by the creation of novel media sensitive to IR radiation[77, 78]. This made it possible to use semiconductor lasers as activating source of radiation[79].

Powdered and film materials based on ion-containing complexes of spiropyrans[80]and also spiropyran copolymers[81] have also been used to record optical data[82] and increase the duration of its storage.

Carboxylatedspiropyrans have been used for determination of the activity of peroxidase[83] and in systems for the determination of low level NO_2content in the environment[84].

Spiropyran finds widespread use as molecular logic devices[85]including the production of nanostructured films from biopolymers[86],thermo/photochromic and electrooptical devices[87], molecular and supramolecular logic switches[88], photoswitches[89] and multifunctional artificial receptors[90]. Photochromic spiropyrans are promising for use in the creation of various types of optical memory[91] in quantum computers[92].

Chapter 2
PLAN OF WORK

It was planned to achieve the target synthesis and silica encapsulation of novel spiropyran based thermochromic materials as temperature sensors.

- To achieve this objective, firstly various N- substituted indoles were synthesized by using 2,3,3-trimethylindolene and alkyl halides or α-halo esters e.g ethyl bromide, n-propyl bromide, n-butyl bromide, iso-butyl bromide, methyl bromo acetate and ethyl bromo acetate.

- The substituted indoles were then reacted with the nitro substituted 2-Hydroxy benzaldehyde, to get the respective spiropyrans. The 2-hydroxy benzaldehyde used were,

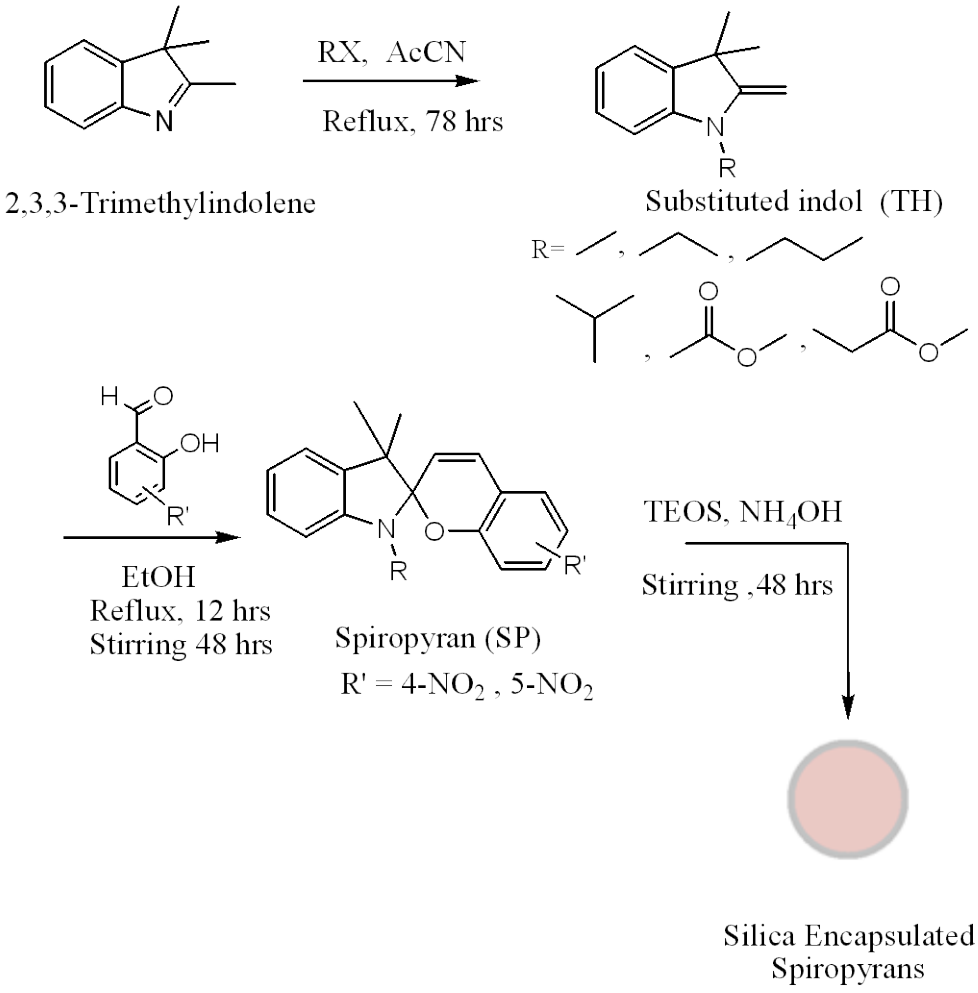
  - 4-Nitro-2-hydroxy benzaldehyde
  - 5-Nitro-2-hydroxy benzaldehyde

- These spiropyrans were encapsulated in silica meso spheres using tetraethylortho silicate as silica precursor.

In the third step, it was decided to encapsulate the fully characterized novel spiropyrans dyes in the silica shells through polymerization of tetraethyl orthosilicate in a basic media. We had also planned the tests of thermochromic behavior of spiropyran dyes in aq/ethanol solution.

The silica encapsulation was proposed for an ease of practical application of material over a wide range of surfaces without the effect of moisture and pH on the structure of the dye and henceforth the thermochromic behavior.

Synthetic Scheme:

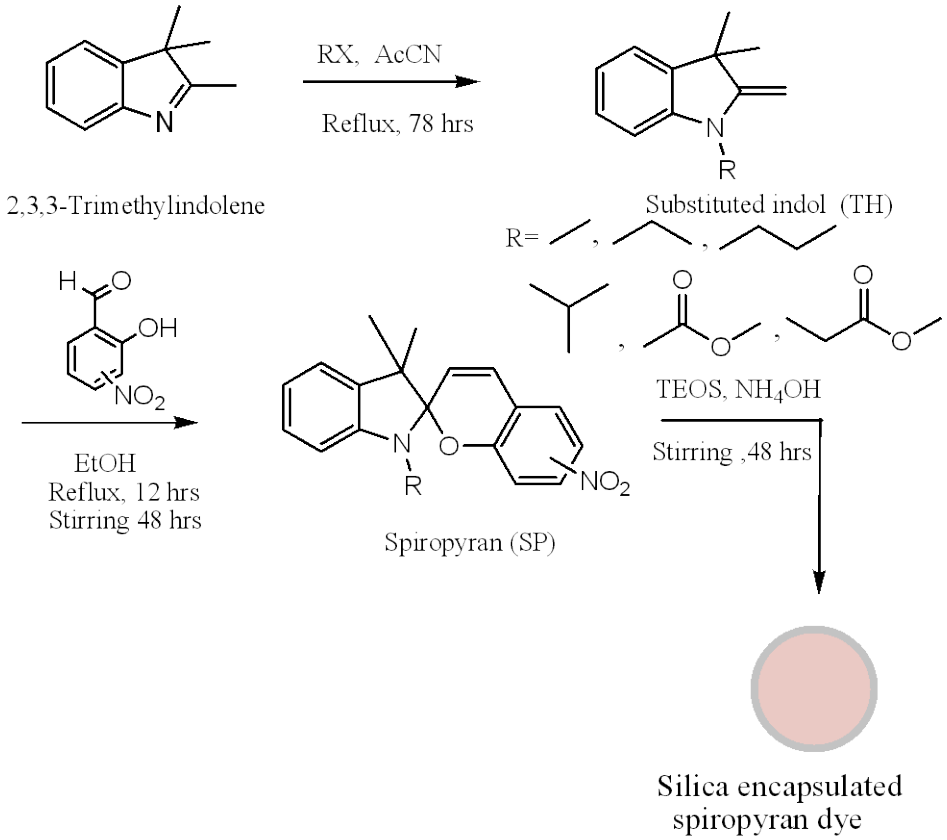


The focus of research work presented in this thesis is the synthesis of silica encapsulated spiropyran based thermochromic material.

We have substituted indole with six different groups (ethyl, propyl, butyl, isobutyl, methyl acetate and ethyl acetate) and then these substituted indoleswere used to synthesis the spiropyrans.

3.1 Synthesisof ThermochromicDye

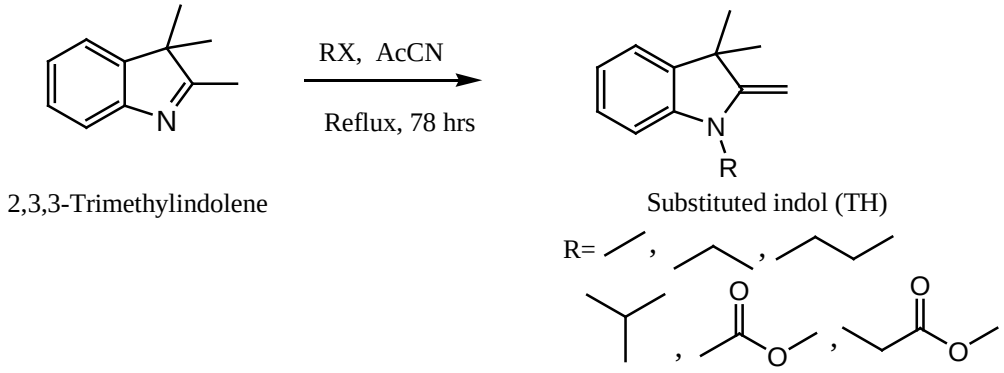
Spiropyrans were synthesized by the reaction of 2,3,3-trimethyl-3*H*-indole with the respective alkyl halide or α-halo esters, followed by the reaction with 2-hydroxy-4-nitrobenzaldehyde or 2-hydroxy-5-nitrobenzaldehyde.General scheme for synthesis of substituted indole, spiropyran and its encapsulation is given in **Scheme 3.1**.



Scheme3.1: General scheme for synthesis of substituted indole, spiropyranand its encapsulation

3.1.1 Synthesis of Substituted Indole (TH)

For the preparation of spiropyrans to be encapsulated in silica,2,3,3-trimethyl-3*H*-indolewas substituted by using alkyl halide or α-halo esters**(Scheme 3.2)**.

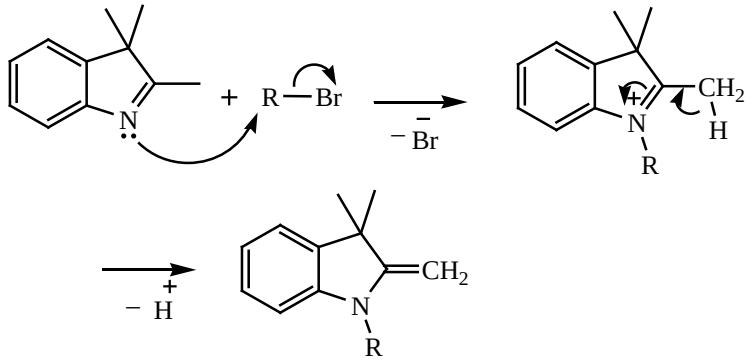


2,3,3-Trimethylindolene

Substituted indol (TH)

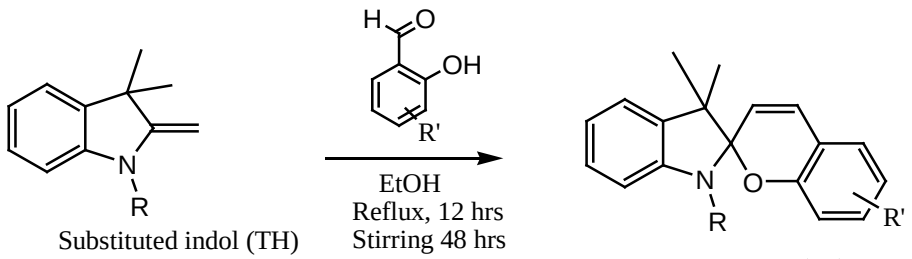
Scheme 3.2: Synthesis of substituted indole (TH)

Mechanism



3.1.2Synthesis of Spiropyran

Substituted indoles wereconverted to spiropyran (SP) by refluxing them with2-hydroxy-4-nitrobenzaldehyde or 2-hydroxy-5-nitrobenzaldehydein dry, distilled ethanol**(Scheme 3.3)**.



Substituted indol (TH)

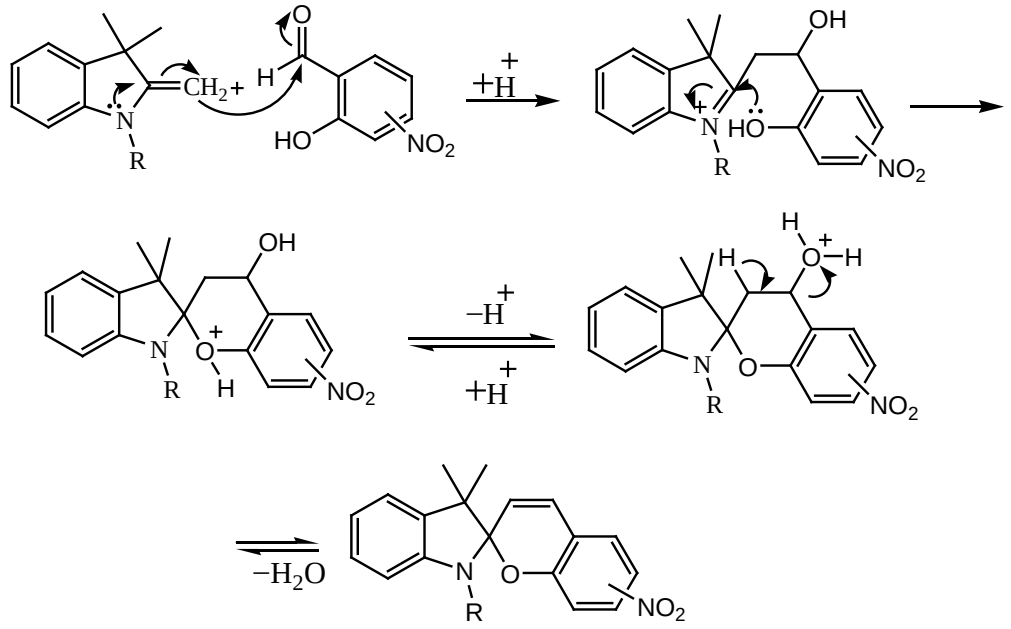
R= Alkyl, Ester

Spiropyran (SP)

R'= 4-NO_2, 5-NO_2

Scheme 3.3: Synthesis of spiropyrans (SP**)**

Mechanism



3.1.2.1 Characterization of 1′,3′-dihydro-3′,3′-dimethyl-1′-ethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-1)

Physical constants of SP-1 are given in **table3.1**.

Table 3.1: Physical constants of SP-1

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-1	Dark khaki solid	0.40	90	165

* *n*-hexane: ethyl acetate(9:1)

3.1.2.1aSpectroscopic analysis of SP-1

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In IR spectrum absorptions in the olefinic region indicated the formation of product. IR spectral data of the compound **SP-1** is given in the **table3.2**.

Table 3.2: IR data of SP-1

Code	ū (cm^{-1})					
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C-O**
SP-1	2967, 2867	3070	1650	1607	1332	1213

3.1.2.1b ^{1}H-NMR and ^{13}C-NMR analysis of SP-1

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.00ppm and 7.20ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.06 ppm and 122.12ppm.Substitution wasconfirmed by the peaks at 3.16 ppm for protons of –NC*H*$_2$CH$_3$and 1.085ppm for–NCH$_2$C*H*$_3$ in ^{1}H-NMR and the peaks at 45.07 ppm and 14.05 ppm in ^{13}C-NMR.^{1}H-NMR and ^{13}C-NMR data is given in **table3.3**.

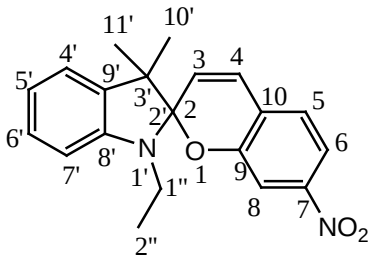


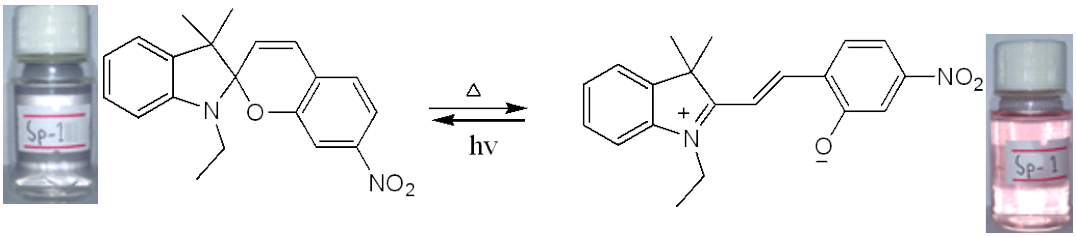
Table3.3: ^{1}H-NMR and ^{13}C-NMR data of SP-1

Proton	δ(ppm),multiplicityand coupling constants *J* (Hz)	Carbons	δ(ppm)
--	--	**C-2**	106.88
H-3	6.00 (1H,d,*J*=10.5Hz)	**C-3**	128.06
H-4	7.20 (1H,d,*J*=10.5Hz)	**C-4**	122.12
H-5	7.11 (1H,d,*J*=8.4Hz)	**C-5**	128.51
H-6	8.00, 7.98 (1H,dd,*J*=9,2.7Hz)	**C-6**	115.87

--	--	**C-7**	140.86
H-8	8.22 (1H,d,*J*=2.7Hz)	**C-8**	106.94
--	--	**C-9**	159.70
--	--	**C-10**	122.31
--	--	**C-2'=C-2**	106.88
--	--	**C-3'**	052.72
H-4'	6.86 (1H,d, *J*=9Hz)	**C-4'**	123.30
H-5'	7.11 (1H,t,*J*=8.9Hz)	**C5'**	119.34
H-6'	6.77 (1H,t,*J*=8.7Hz)	**C-6'**	126.19
H-7'	6.60 (1H,d,*J*=8.5Hz)	**C-7'**	119.18
--	--	**C-8'**	147.28
--	--	**C-9'**	136.03
H-10'	1.08 (3H,s)	**C-10'**	019.97
H-11'	1.20 (3H,s)	**C-11'**	022.11
H-1''	3.16 (1H,q,*J*=7.2Hz)	**C-1''**	045.07
H-2''	1.08 (3H,t,*J*=7.5Hz)	**C-2''**	014.05

3.1.2.1c UV-Visible spectroscopy of SP-1

The UV-Visible spectroscopy of SP-1 was carried out to study the thermochromic behavior of the spiropyrans and to analyze the change of absorbance peak with change in temperature. As the temperature increases with regular intervals, the absorbance increases, which confirm the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC)(**Scheme 3.4)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.4: Conversion ofSP-1 from SP form to MC form

The absorbance versus wavelength spectrum of SP-1 was taken in 1:1 ethanol water mixture. The absorbance spectrum of SP-1 is given in **figure 3.1.**

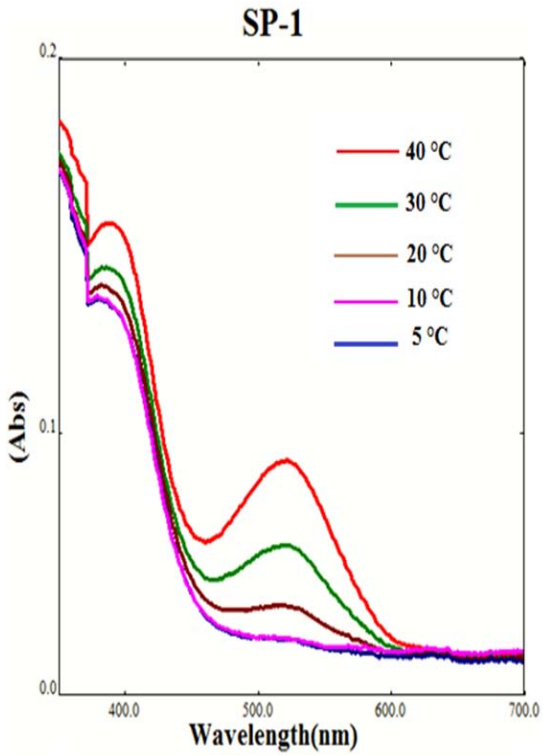


Figure 3.1: Absorbance versus wavelength spectrum of SP-1

3.1.2.2 Characterization of 1′,3′-dihydro-3′,3′-dimethyl-1′-propyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-2)

Physical constants of SP-2 are given in **table3.4**.

Table 3.4: Physical constants of SP-2

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-2	Ecru solid	0.47	92	149

* *n*-hexane: ethyl acetate (9:1)

3.1.2.2aSpectroscopic analysis of SP-2

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound **SP-2**is given in the **table 3.5**.

Table 3.5: IR data of SP-2

Code	$\bar{\upsilon}$ (cm^{-1})					
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C-O**
SP-2	2957, 2876	3080	1648	1608	1333	1209

3.1.2.2b^{1}H-NMR and ^{13}C-NMR analysis of SP-2

The formation of product wasconfirmed by^{1}H-NMR and ^{13}C-NMR analysis. The characteristic peak of –CH=CH– in^{1}H-NMR spectrum appeared as two doublets at 6.00 ppm and 7.20 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.06 ppm and 122.12 ppm. The substitution was confirmed by the peak at 3.08 ppm for –NCH_2CH$_2$–in ^{1}H-NMR and the peak at 45.07 ppm in ^{13}C-NMR. ^{1}H-NMR and ^{13}C-NMR data is given in **table3.6**.

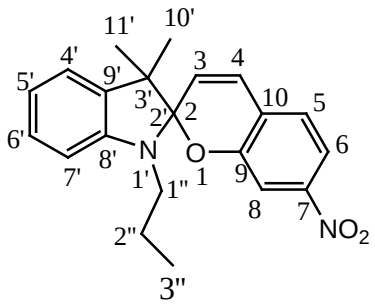


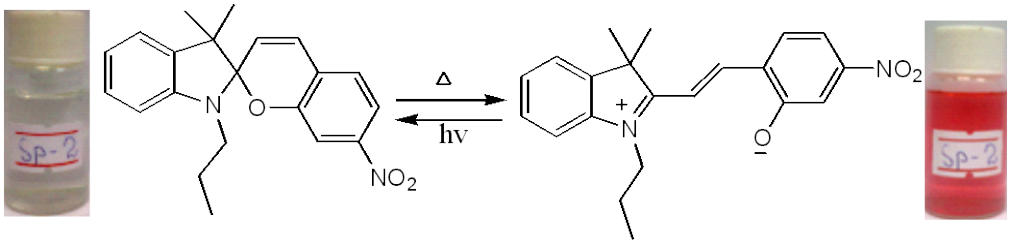
Table3.6: ^{1}H-NMR and ^{13}C-NMR dataof SP-2

Proton	**δ(ppm),multiplicity and coupling constants *J* (Hz)**	**Carbons**	**δ(ppm)**
--	**--**	**C-2**	106.88
H-3	6.00 (1H,d,*J*=10.5Hz)	**C-3**	128.06
H-4	7.20 (1H,d,*J*=10.5Hz)	**C-4**	122.12
H-5	7.11 (1H,d, *J*=8.4Hz)	**C-5**	128.51
H-6	7.99, 7.97 (1H,dd,*J*=9,2.7Hz)	**C-6**	115.87
--	**--**	**C-7**	140.86
H-8	8.21 (1H,d, *J*=2.7Hz)	**C-8**	106.94
--	**--**	**C-9**	159.70
--	**--**	**C-10**	122.31
--	**--**	**C-2'=C-2**	106.88
--	**--**	**C-3'**	052.72
H-4'	6.86 (1H,d,*J*=9Hz)	**C-4'**	123.30
H-5'	7.11, 7.06 (1H,dd,*J*=8.4, 6.6Hz)	**C5'**	119.34
H-6'	6.77 (1H,t, *J*=7.5Hz)	**C-6'**	126.19
H-7'	6.59 (1H,d,*J*=7.5Hz)	**C-7'**	119.18

--	--	**C-8'**	147.28
--	--	**C-9'**	136.03
H-10'	1.10 (3H,s)	**C-10'**	019.97
H-11'	1.19 (3H,s)	**C-11'**	022.11
H-1''	3.08 (2H,t,*J*=7.2Hz)	**C-1''**	045.07
H-2''	1.607 (2H, m, *J*=7.5Hz)	**C-2''**	026.32
H-3''	0.84 (3H,t,*J*=7.2Hz)	**C-3''**	011.97

3.1.2.2c UV-Visible spectroscopy of SP-2

Thermochromic behavior of SP-2 was studied by using UV-Visible spectroscopy.This behavior of spiropyrans wasanalyzed by observing the change of absorbance peak with change in temperature. As the temperatureincreases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC) (**Scheme 3.5)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.5: Conversion of SP-2 from SP form to MC form

The absorbance versus wavelength spectrum of SP-2 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-2 is given in **figure 3.2.**

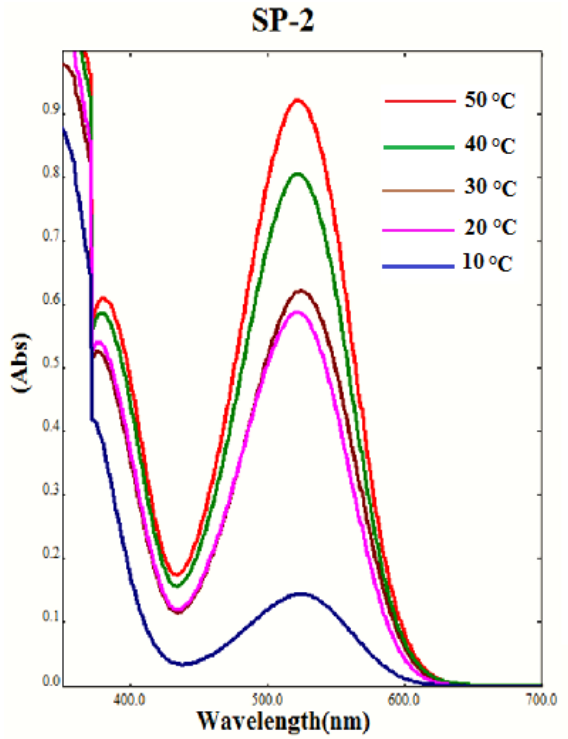


Figure 3.2: Absorbance versus wavelength spectrum of SP-2

3.1.2.3 Characterization of 1′,3′-dihydro-3′,3′-dimethyl-1′-butyl-7-nitro-spiro[2*H*-1-benzopyran-2, 2′-(2*H*)-indole](SP-3)

Physical constants of SP-3 are given in **table3.7**.

Table 3.7: Physical constants of SP-3

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-3	Citrine solid	0.60	83	170

* *n*-hexane: ethyl acetate (9:1)

3.1.2.3aSpectroscopic analysis of SP-3

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-3**is given in the **table 3.8**.

Table 3.8: IR data of SP-3

Code	ū (cm^{-1})					
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C-O**
SP-3	2960, 2850	3075	1652	1608	1325	1213

3.1.2.3b ^{1}H-NMR and ^{13}C-NMR analysis of SP-3

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.00 ppm and 7.21 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.06 ppm and 122.12 ppm. The n-buthylsubstitution was confirmed by the peak at 3.21 ppm for protons of –NCH_2CH$_2$–in ^{1}H-NMR and the peak at 48.90 ppm in ^{13}C-NMR.^{1}H-NMR and ^{13}C-NMR data is given in **table3.9**.

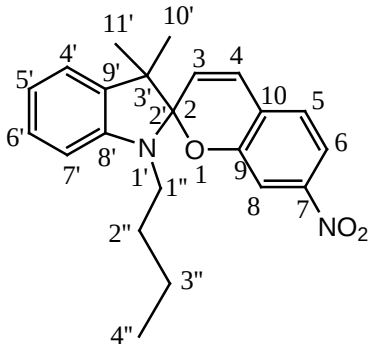


Table3.9: ^{1}H-NMR and ^{13}C-NMR data of SP-3

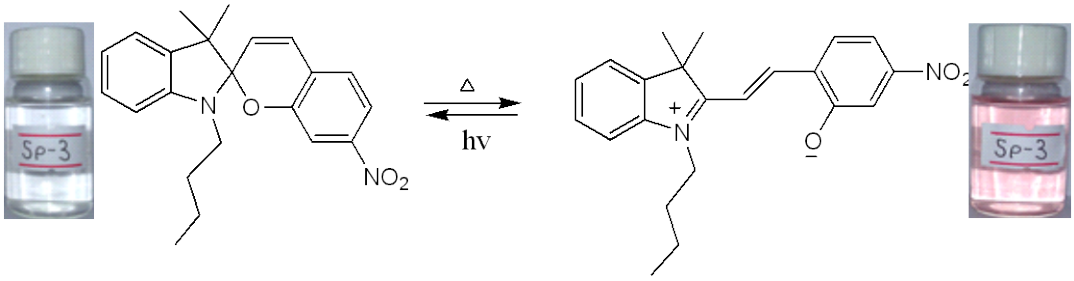
Proton	δ(ppm),multiplicity and coupling constants*J*(Hz)	Carbons	δ(ppm)
--	--	**C-2**	106.88
H-3	6.00 (1H,d,*J*=10.5Hz)	**C-3**	128.06
H-4	7.21(1H,d,*J*=10.5Hz)	**C-4**	122.12

H-5	8.22(1H, d, *J*=2.7Hz)	**C-5**	128.53
H-6	8.00,7.98 (1H,dd,*J*=9,2.7Hz)	**C-6**	115.87
--	**--**	**C-7**	141.09
H-8	7.12 (1H, d,*J*=9Hz)	**C-8**	107.01
--	**--**	**C-9**	158.09
--	**--**	**C-10**	122.13
--	**--**	**C-2'=C-2**	106.88
--	**--**	**C-3'**	051.99
H-4'	6.86 (1H,d,*J*=9 Hz)	**C-4'**	126.19
H-5'	6.77 (1H, t, *J*=9Hz)	**C5'**	119.96
H-6'	7.10 (1H, t,*J*= 9Hz)	**C-6'**	127.95
H-7'	6.59 (1H,d,J= 9Hz)	**C-7'**	119.87
--	**--**	**C-8'**	146.20
--	**--**	**C-9'**	136.01
H-10'	1.20 (3H,s)	**C-10'**	018.03
H-11'	1.24 (3H,s)	**C-11'**	019.99
H-1''	3.21 (2H,sextet,*J*=7.5Hz)	**C-1''**	048.90
H-2''	1.52 (2H,quintet,*J*=7.5Hz)	**C-2''**	029.40
H-3''	1.28 (2H,sextet,*J*=7.5Hz)	**C-3''**	019.04
H4''	0.83 (3H, t,*J*=7.5Hz)	**C-4''**	014.03

3.1.2.3c UV-Visible spectroscopy of SP-3

UV-Visible spectroscopy of SP-3 was carried out to study the thermochromic behavior of the spiropyrans and to analyze the change of

absorbance peak with change in temperature. As the temperatureincreases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC) **(Scheme 3.6).**



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.6: Conversion of SP-3 from SP form to MC form

The absorbance versus wavelength spectrum of SP-3 was taken in 1:1 ethanol water mixture. The absorbance spectrum of SP-3 is given in **(figure 3.3).**

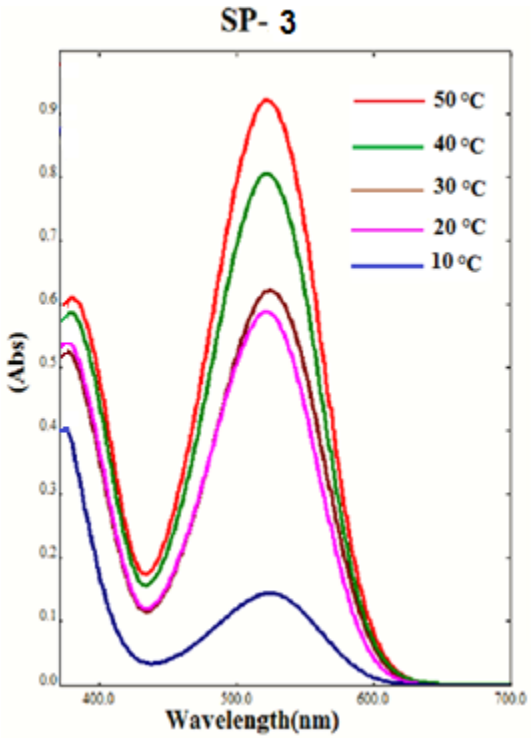


Figure 3.3: Absorbance versus wavelength spectrum of SP-3

3.1.2.4Characterization of 1′,3′-dihydro-1′-(1-methylpropyl)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-4)

Physical constants of SP-4 are given in **table3.10**.

Table 3.10: Physical constants of SP-4

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-4	Dark golden rod solid	0.52	80	178

* *n*-hexane: ethyl acetate (9:1)

3.1.2.4aSpectroscopic analysis of SP-4

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-4**is given in the **table 3.11**.

Table 3.11: IR data of SP-4

Code	$\bar{\upsilon}$ (cm^{-1})					
	sp^3C-H	Ar-H	C=C (Aliphatic)	C=C (Aromatic)	C-N	C-O
SP-4	2963, 2865	3080	1649	1611	1335	1210

3.1.2.4b^{1}H-NMR and ^{13}C-NMR analysis SP-4

The formation of product wasconfirmed by ^{1}H-NMR and ^{13}C-NMR analysis. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.03 ppm and 7.25 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.06 ppm and 122.12 ppm. The substitution of isobutyl group was confirmed by the peak at 2.79 ppm for protons of –NC*H*CH_2– in ^{1}H-NMR and the peak at 49.83 ppm in ^{13}C-NMR. ^{1}H-NMR and ^{13}C-NMR data is given in **table3.12**.

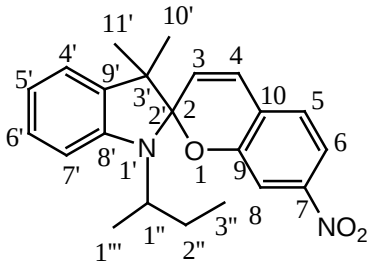


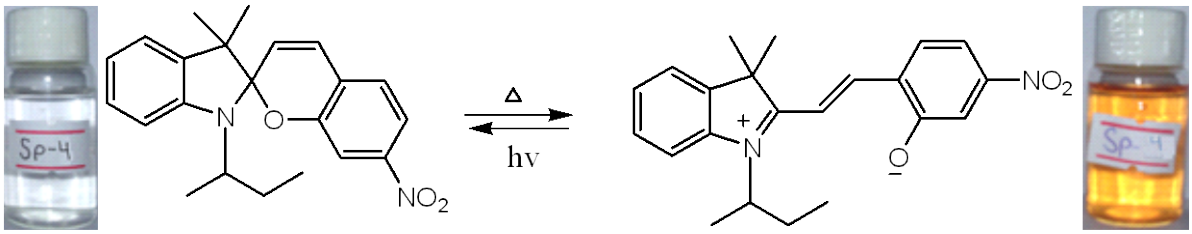
Table3.12: ^{1}H-NMR and ^{13}C-NMR data of SP-4

Proton	**δ(ppm),multiplicity and coupling constants *J*(Hz)**	**Carbons**	**δ(ppm)**
--	**--**	**C-2**	106.08
H-3	6.03 (1H,d,*J*=10.5Hz)	**C-3**	128.06
H-4	7.25 (1H,d,*J*=10.5Hz)	**C-4**	122.12
H-5	8.03 (1H, d, *J*=3Hz)	**C-5**	128.53
H-6	8.13,8.11 (1H,dd,*J*=9,3Hz)	**C-6**	115.87
--	**--**	**C-7**	141.09
H-8	8.21 (1H, d,*J*=3Hz)	**C-8**	107.01
--	**--**	**C-9**	159.63
--	**--**	**C-10**	122.13
--	**--**	**C-2'=C-2**	106.08
--	**--**	**C-3'**	052.70
H-4'	6.89(1H,d,*J*=9Hz)	**C-4'**	123.33
H-5'	6.83 (1H, t, *J*=8.9Hz)	**C5'**	119.43
H-6'	7.10(1H, t,*J*= 9Hz)	**C-6'**	127.01
H-7'	6.59 (1H,d,*J*= 9Hz)	**C-7'**	119.18
--	**--**	**C-8'**	147.52

--	--	**C-9'**	136.05
H-10'	1.09(3H,s)	**C-10'**	019.98
H-11'	1.13 (3H,s)	**C-11'**	022.11
H-1''	2.79(1H,sextet,*J*=7.8Hz)	**C-1''**	049.83
H-2''	1.53(2H,quintet,*J*=7.5Hz)	**C-2''**	029.47
H-3''	0.85(3H,t,*J*=7.5Hz),	**C-3''**	014.83
H-1'''	1.25 (3H, d,*J*=7.5Hz)	**C-1'''**	021.09

3.1.2.4cAbsorbancespectroscopy of SP-4

Thermochromic behavior of SP-4 was studied by using UV-Visible spectroscopy. This behavior of spiropyrans was analyzed by observing the change of absorbance peak with change in temperature. As the temperature increases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC)**(Scheme 3.7)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.7: Conversion of SP-4 from SP form to MC form

The absorbance versus wavelength spectrum of SP-4 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-3 is given in **figure 3.4.**

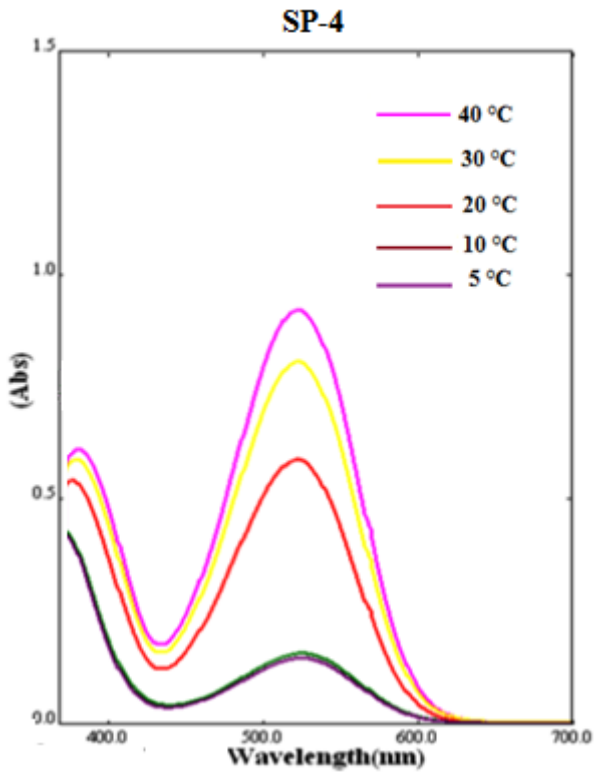


Figure 3.4: Absorbance versus wavelength spectrum of SP-4

3.1.2.5Characterization of 1′,3′-dihydro-1′-(1-methylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-5)

Physical constants of SP-5 are given in below in **table3.13**.

Table 3.13: Physical constants of SP-5

Code	**Physical Appearance**	**R_f*value**	**% Yield**	**M.P(°C)**
SP-5	Bright Baroon solid	0.50	80	166

* *n*-hexane: ethyl acetate (9:1)

3.1.2.5aSpectroscopic analysis of SP-5

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-5**is given in the **table 3.14**.

Table 3.14: IR data of SP-5

Code	ū (cm^{-1})							
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C=O**	**C-O Ester**	**C-O Ether**
SP-5	2957, 2850	3076	1656	1607	1332	1740	1190	1212

3.1.2.5b ^{1}H-NMR and ^{13}C-NMR analysis of SP-5

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 5.99 ppm and 6.58 ppm for two protons H-3 and H-4 respectively. In ^{13}C-NMR, these carbons (C-3 and C-4) appeared at 128.06 ppm and 122.12 ppm. The substitution was confirmed by the peak for the methylene proton from N-substituted moiety–$NCH_{2(}C=O)$– appeared at 2.75 ppm. Other^{13}C-NMR peak, however, was observed at52.07 ppm for the same carbon. ^{1}H-NMR and ^{13}C-NMR data is providedin **table3.15**.

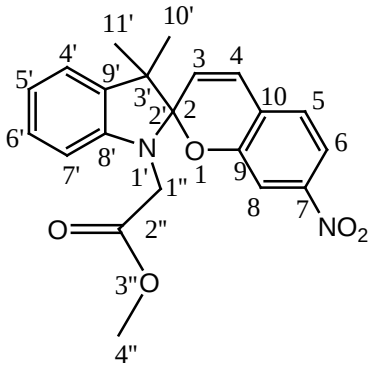


Table3.15: ^{1}H-NMR and ^{13}C-NMR data of SP-5

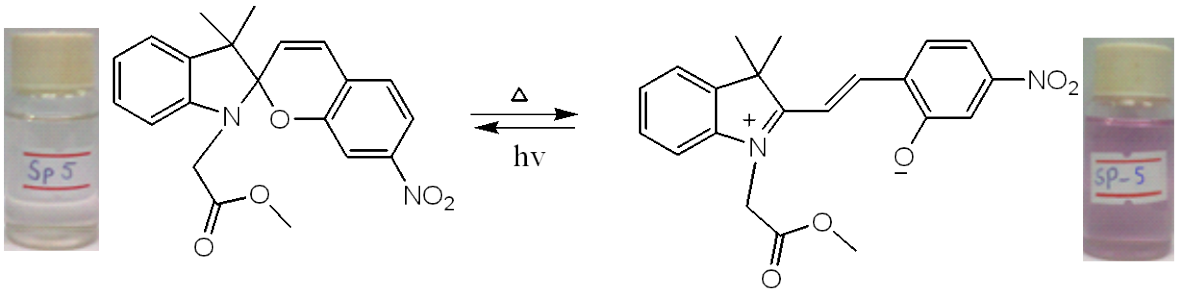
Proton	δ(ppm),multiplicity and coupling constants *J*(Hz)	Carbons	δ(ppm)
--	--	**C-2**	106.88
H-3	5.99 (1H, d, *J*=10.5Hz)	**C-3**	128.06
H-4	6.58 (1H, d, *J*=10.5Hz)	**C-4**	122.12

H-5	7.15 (1H, d, *J*=8.6Hz)	**C-5**	128.51
H-6	8.05,8.03 (1H, dd, *J*=9,2.7Hz)	**C-6**	115.87
--	**--**	**C-7**	140.86
H-8	8.12(1H,d,*J*=2.7Hz)	**C-8**	106.94
--	**--**	**C-9**	159.70
--	**--**	**C-10**	122.31
--	**--**	**C-2'=C-2**	106.88
--	**--**	**C-3'**	052.72
H-4'	6.81(1H,d,*J*=9Hz)	**C-4'**	123.30
H-5'	7.09 (1H,t,*J*=8.9Hz)	**C5'**	119.34
H-6'	6.84 (1H,t,*J*=8.7Hz)	**C-6'**	126.19
H-7'	6.60(1H,d,*J*=8.5Hz)	**C-7'**	119.18
--	**--**	**C-8'**	147.28
--	**--**	**C-9'**	136.03
H-10'	1.19(3H,s)	**C-10'**	019.97
H-11'	1.30 (3H,s)	**C-11'**	022.11
H-1''	2.75(2H,s)	**C-1''**	52.07
--	**--**	**C-2''**	172.02
H-4''	1.08(3H,t,*J*=7.5Hz)	**C-4''**	054.00

3.1.2.5cAbsorbancespectroscopy of SP-5

Absorbancespectroscopy of SP-5 was carried out to study the thermochromic behavior of the spiropyrans and to analyze the change of absorbance peak with change in temperature. As the temperature increases with regular intervals, the absorbance increases, which confirm the conversion

of colorless spirocyclic form (SP) to colored merocyanin form (MC) **(Scheme 3.8)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.8: Conversion of SP-5 from SP form to MC form

The absorbance versus wavelength spectrum of SP-5 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-3 is given in **figure 3.5.**

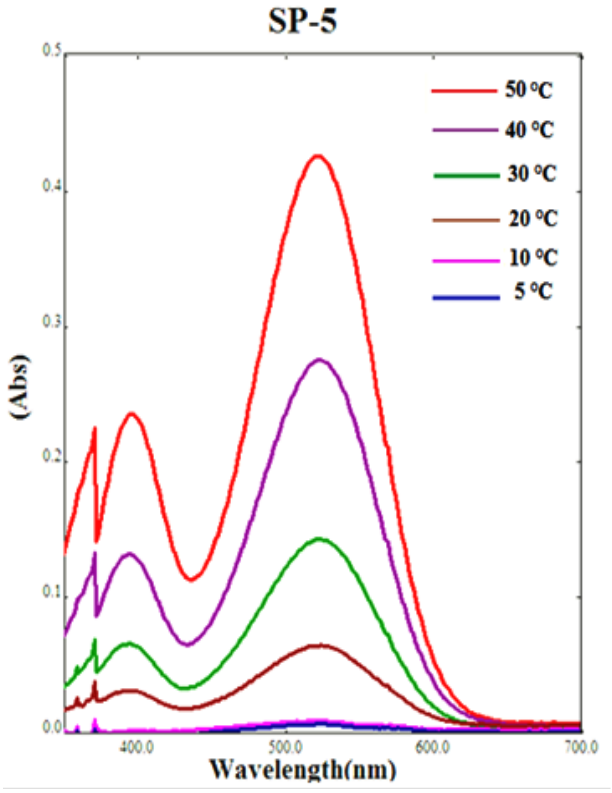


Figure 3.4: Absorbance versus wavelength spectrum of SP-5

3.1.2.6 Characterization of 1′,3′-dihydro-1′-(1-ethylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-6)

Physical constants of SP-6 are given below in**table3.16**.

Table 3.16: Physical constants of SP-6

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-6	Light khaki solid	0.46	79	112

* *n*-hexane: ethyl acetate (9:1)

3.1.2.6aSpectroscopic analysis of SP-6

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-6**is given in the **table 3.17**.

Table 3.17: IR data of SP-6

Code	$\bar{\upsilon}$ (cm^{-1})							
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C=O**	**C-O Ester**	**C-O Ether**
SP-6	2968, 2869	3078	1639	1605	1336	1746	1190	1211

3.1.2.6b^{1}H-NMR and ^{13}C-NMR analysis of SP-6

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 5.92 ppm and 7.22 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 127.96 ppm and 121.22 ppm. The substitution was confirmed by the peak at 3.08 for protons of –NCH_2CH_2– in ^{1}H-NMR and the peak at 44.67 ppm in ^{13}C-NMR. ^{1}H-NMR and ^{13}C-NMR data is given in **table3.18**.

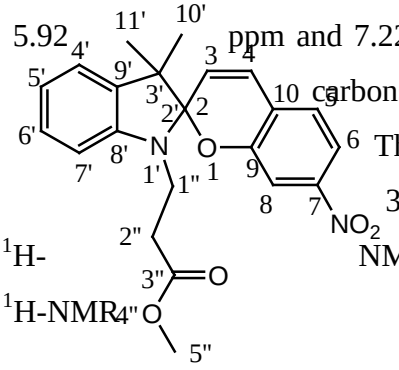


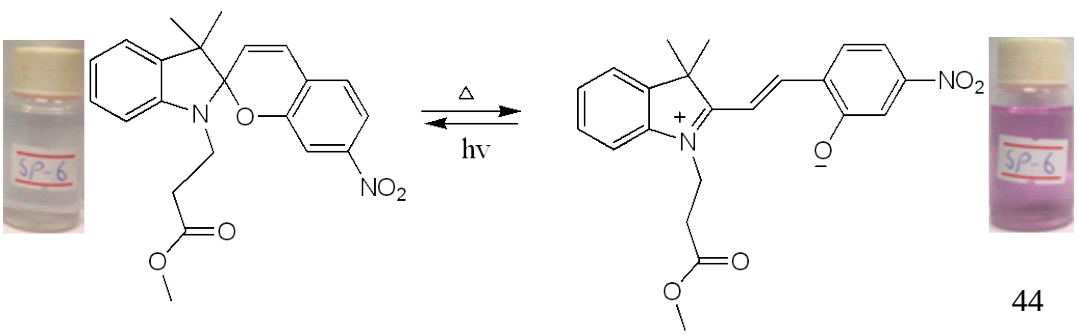
Table3.18: ^{1}H-NMR and ^{13}C-NMR data of SP-6

Proton	**δ(ppm),multiplicity and coupling constants*J*(Hz)**	**Carbons**	**δ(ppm)**
--	**--**	**C-2**	105.78
H-3	5.92 (1H,d,*J*=10.5Hz)	**C-3**	127.96
H-4	7.22 (1H,d,*J*=10.5Hz)	**C-4**	122.22
H-5	6.86 (1H,d,*J*=9Hz)	**C-5**	129.18
H-6	8.01,7.99 (1H, dd, *J*=9,2.7Hz)	**C-6**	115.87
--	**--**	**C-7**	141.04
H-8	8.22 (1H, d, *J*=2.7Hz)	**C-8**	107.27
--	**--**	**C-9**	159.34
--	**--**	**C-10**	122.19

--	--	**C-2'=C-2**	105.78
--	--	**C-3'**	052.70
H-4'	7.42 (1H,d,*J*=7.2Hz)	**C-4'**	123.34
H-5'	6.81 (1H, t, *J*=7.8Hz)	**C5'**	119.96
H-6'	7.08 (1H, t. *J*= 7.5Hz)	**C-6'**	126.20
H-7'	6.69 (1H,d,*J*=7.5Hz)	**C-7'**	119.12
--	--	**C-8'**	146.25
--	--	**C-9'**	135.60
H-10'	1.09 (3H,s)	**C-10'**	014.41
H-11'	1.13 (3H,s)	**C-11'**	019.93
H-1''	4.03 (2H,t,*J*=6.9Hz)	**C-1''**	044.67
H-2''	4.00 (2H,t,*J*=6.9Hz)	**C-2''**	026.47
--	--	**C-3''**	170.17
H-5''	1.22 (3H, s)	**C-5''**	061.03

3.1.2.6cAbsorbancespectroscopy of SP-6

Thermochromic behavior of SP-6 was studied by using UV-Visible spectroscopy. This behavior of spiropyrans was analyzed by observing the change of absorbance peak with change in temperature. As the temperature increases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC)**(Scheme 3.9)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.9: Conversion of SP-6 from SP form to MC form

The absorbance versus wavelength spectrum of SP-6 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-6 is given in **figure 3.6.**

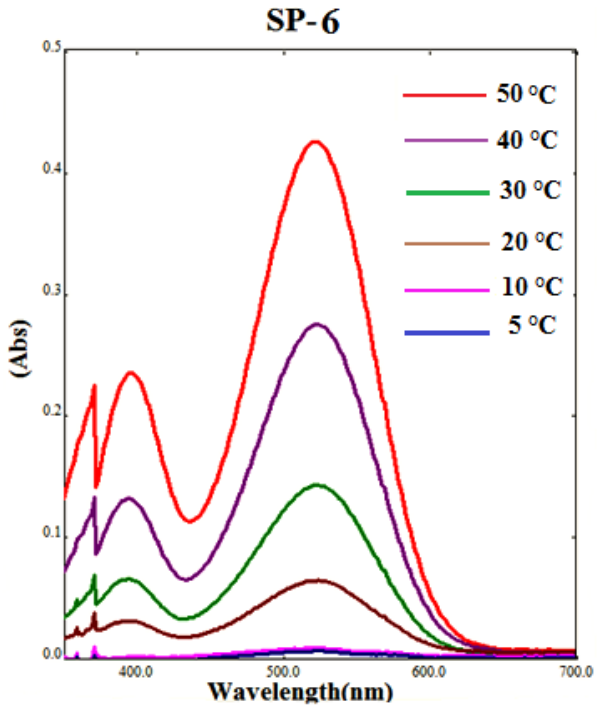


Figure 3.6: Absorbance versus wavelength spectrum of SP-6

3.1.2.7 Characterization of 1′,3′-dihydro-3′,3′-dimethyl-1′-ethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-7)

Physical constants of SP-7 are given below in **table3.19**.

Table 3.19: Physical constants of SP-7

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-7	khaki	0.48	79	160

	solid			

* *n*-hexane: ethyl acetate (9:1)

3.1.2.7aSpectroscopic analysis of SP-7

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-7**is given in the **table 3.20**.

Table 3.20: IR data of SP-7

Code	$\bar{\upsilon}$ (cm^{-1})					
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C-O**
SP-7	2968,2870	3075	1651	1610	1332	1212

3.1.2.7b^{1}H-NMR and ^{13}C-NMR analysis of SP-7

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.00 ppm and 7.20 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.10 ppm and 122.31 ppm. The substitution was confirmed by the peaks at 3.16 ppm protons of –NCH_2CH$_3$and 1.08 ppm for –NCH$_2$CH_3 in ^{1}H-NMR. The peaks at 45.03 ppm and 14.77 ppm in ^{13}C-NMR. ^{1}H-NMR and ^{13}C-NMR data is given in **table3.21**.

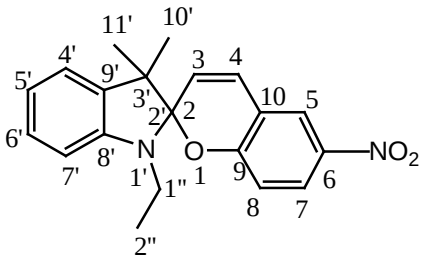


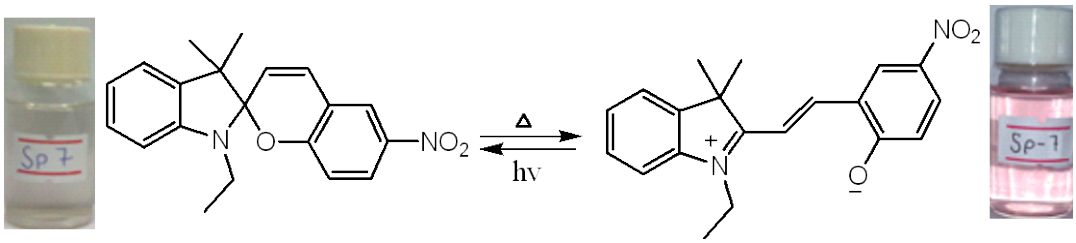
Table3.21: ^{1}H-NMR and ^{13}C-NMR data of SP-7

Proton	**δ(ppm),multiplicity and coupling constants *J*(Hz)**	**Carbons**	**δ(ppm)**

--	**--**	**C-2**	105.90
H-3	6.00(1H, d, *J*=10.5Hz)	**C-3**	128.10
H-4	7.20(1H, d, *J*=10.5Hz)	**C-4**	122.31
H-5	8.22 (1H, d, *J*=3Hz)	**C-5**	123.25
--	**--**	**C-6**	140.44
H-7	8.01,7.98 (1H, dd, *J*=9,3Hz)	**C-7**	122.11
H-8	7.11 (1H, d, *J*=8.7Hz)	**C-8**	115.81
--	**--**	**C-9**	160.01
--	**--**	**C-10**	119.21
--	**--**	**C-2'=C-2**	105.90
--	**--**	**C-3'**	44.99
H-4'	6.86 (1H, d, *J*=9Hz)	**C-4'**	123.31
H-5'	6.77 (1H, t, *J*=8.9Hz)	**C5'**	119.34
H-6'	7.10 (1H, t, *J*=9Hz)	**C-6'**	126.19
H-7'	6.60 (1H, d, *J*=9Hz)	**C-7'**	106.94
--	**--**	**C-8'**	147.31
--	**--**	**C-9'**	128.48
H-10'	1.08 (3H, s)	**C-10'**	019.99
H-11'	1.20 (3H, s)	**C-11'**	022.31
H-1''	3.16 (1H, q, *J*=7.2Hz)	**C-1''**	045.03
H-2''	1.08 (3H, t, *J*=7.5Hz)	**C-2''**	014.77

3.1.2.7cAbsorbancespectroscopy of SP-7

Absorbance spectroscopy of SP-7 was carried out to study the thermochromic behavior of the spiropyrans and to analyze the change of absorbance peak with change in temperature. As the temperature increases with regular intervals, the absorbance increases, which confirm the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC) (**Scheme 3.10)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.10: Conversion of SP-7 from SP form to MC form

The absorbance versus wavelength spectrum of SP-7 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-7 is given in **figure 3.7.**

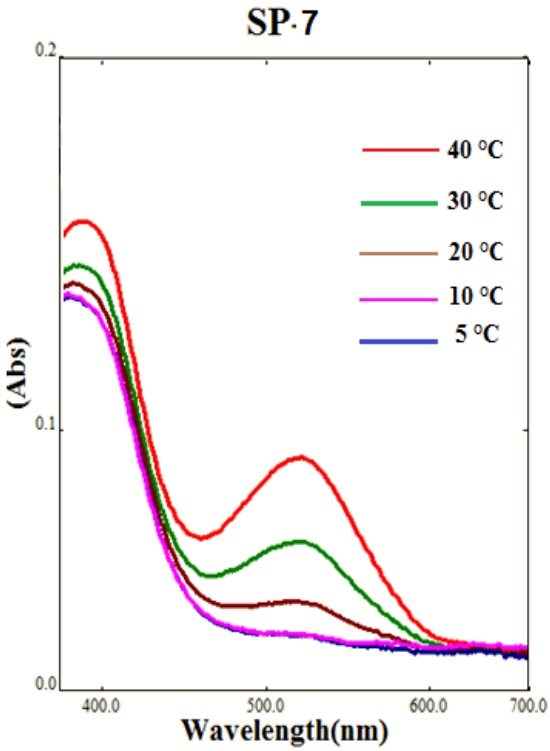


Figure 3.7: Absorbance versus wavelength spectrum of SP-7

3.1.2.8 Characterization of 1′,3′-dihydro-3′,3′-dimethyl-1′-propyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-8)

Physical constants of SP-8 are given in **table3.22**.

Table 3.22: Physical constants of SP-8

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-8	Blue Bellsolid	0.47	88	145

* *n*-hexane: ethyl acetate (9:1)

3.1.2.8aSpectroscopic analysis of SP-8

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-8**is given in the **table 3.23**.

Table 3.23: IR data of SP-8

Code	$\bar{\upsilon}$ (cm^{-1})					
	sp^3C-H	Ar-H	C=C (Aliphatic)	C=C (Aromatic)	C-N	C-O
SP-8	2958, 2866	3076	1649	1608	1333	1209

3.1.2.8b^{1}H-NMR and ^{13}C-NMR analysis of SP-8

The formation of productis confirmed by^{1}H-NMR and ^{13}C-NMR analysis. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum

appeared as two doublets at6.00 ppm and 7.20 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.06 ppm and 122.31 ppm. The substitution was confirmed by the peak at 3.08 ppm for protons of –NC*H*$_2$CH$_2$–in ^{1}H-NMR and the peak at 52.21 ppm in ^{13}C-NMR.^{1}H-NMR and ^{13}C-NMR data is given in **table3.24**.

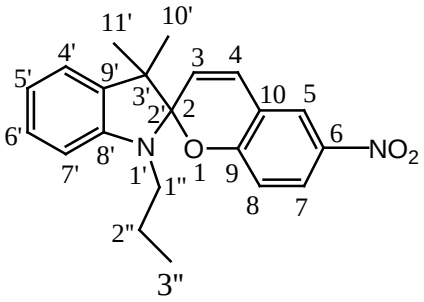


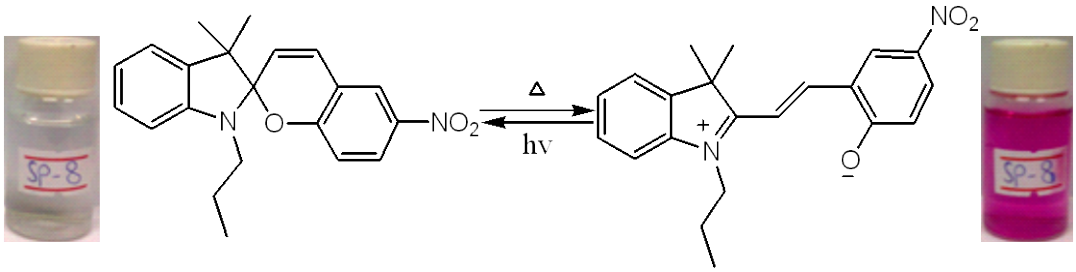
Table3.24: ^{1}H-NMR and ^{13}C-NMR data of SP-8

Proton	**δ(ppm),multiplicity and coupling constants *J*(Hz)**	**Carbons**	**δ(ppm)**
--	**--**	**C-2**	106.88
H-3	6.00(1H,d,*J*=10.5Hz)	**C-3**	128.06
H-4	7.20(1H,d,*J*=10.5Hz)	**C-4**	122.31
H-5	8.22(1H,d,*J*=3Hz)	**C-5**	123.30
H-6	**--**	**C-6**	140.86
H-7	8.01,7.98(1H,dd,*J*=9,3Hz)	**C-7**	122.12
H-8	7.11(1H,d, *J*=8.7Hz)	**C-8**	115.87
--	**--**	**C-9**	159.69
--	**--**	**C-10**	119.18
--	**--**	**C-2'=C-2**	106.88

--	--	**C-3'**	045.07
H-4'	6.86(1H,d, *J*=9Hz)	**C-4'**	123.30
H-5'	6.77(1H,t,*J*=7.2Hz)	**C5'**	119.34
H-6'	7.10(1H,t,*J*=6Hz)	**C-6'**	126.19
H-7'	6.60(1H,d,*J*=8.1Hz)	**C-7'**	106.94
--	--	**C-8'**	147.28
--	--	**C-9'**	128.51
H-10'	1.10(3H,s)	**C-10'**	19.97
H-11'	1.20 (3H,s)	**C-11'**	22.11
H-1''	3.08 (2H,t,*J*=7.5Hz)	**C-1''**	52.21
H-2''	1.59 (1H, m,*J*=7.5Hz)	**C-2''**	26.32
H-3''	0.84 (3H,t,*J*=7.5Hz)	**C-3''**	11.97

3.1.2.8cAbsorbancespectroscopy of SP-8

Thermochromic behavior of SP-8 was studied by using UV-Visible spectroscopy. This behavior of spiropyrans was analyzed by observing the change of absorbance peak with change in temperature. As the temperature increases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC)**(Scheme 3.11)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.11: Conversion of SP-8 from SP form to MC form

The absorbance versus wavelength spectrum of SP-8 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-8 is given in **(figure 3.8).**

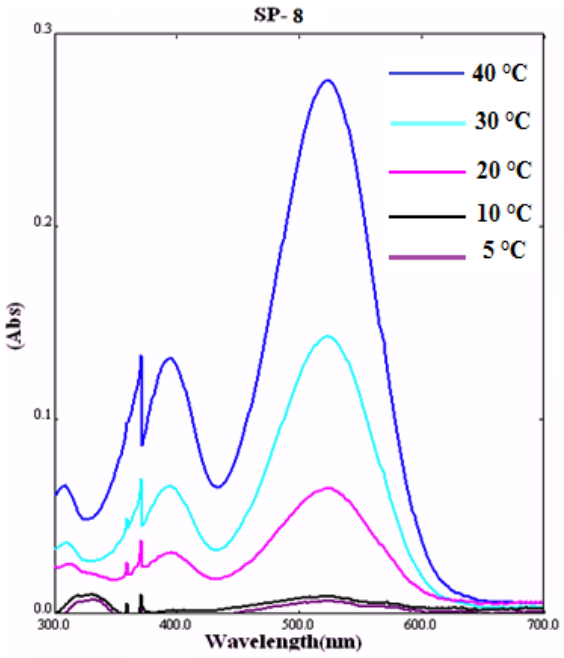


Figure 3.8: Absorbance versus wavelength spectrum of SP-8

3.1.2.9 Characterization of 1′,3′-dihydro-3′,3′-dimethyl-1′-butyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-9)

Physical constants of SP-9 are given in **table3.25**.

Table 3.25: Physical constants of SP-9

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-9	Coral Pink solid	0.40	85	120

* *n*-hexane: ethyl acetate (9:1)

3.1.2.9aSpectroscopic analysis of SP-9

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinicregion indicated the synthesis of product. IR spectral data of the compound**SP-9**is given in the **table 3.26**.

Table 3.26: IR data of SP-9

Code	$\bar{\upsilon}$ (cm^{-1})					
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C-O**
SP-9	2961,2865	3078	1651	1609	1333	1207

3.1.2.9b^{1}H-NMR and ^{13}C-NMR analysis of SP-9

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.00 ppm and 7.21 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 128.06 ppm and 122.19 ppm. The substitution was confirmed by the peak at 3.21 ppm for protons of –NCH_2CH$_2$– in ^{1}H-NMR and the peak at 48.90 ppm in ^{13}C-NMR.^{1}H-NMR and ^{13}C-NMR data is given in **table3.27**.

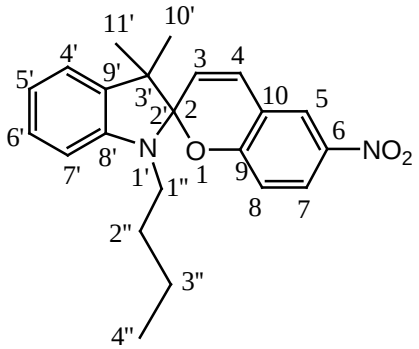


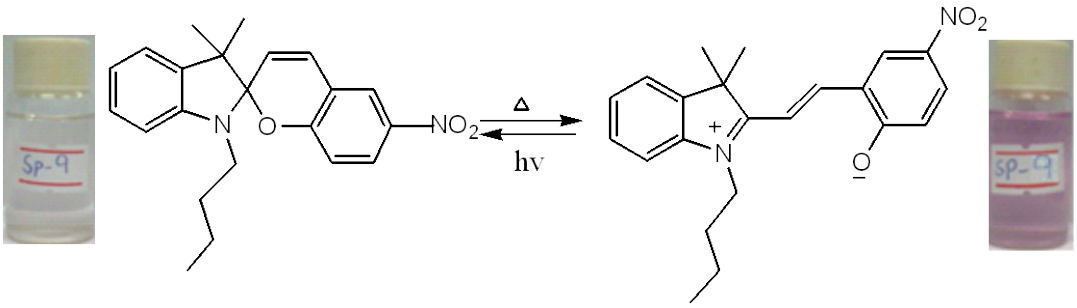
Table3.27: ^{1}H-NMR and ^{13}C-NMR data of SP-9

Proton	**δ(ppm),multiplicity and coupling constants *J*(Hz)**	**Carbons**	**δ(ppm)**

--	**--**	**C-2**	105.08
H-3	6.00 (1H,d,*J*=10.5Hz)	**C-3**	129.10
H-4	7.21(1H,d,*J*=10.5Hz)	**C-4**	121.9
H-5	8.22 (1H, d, *J*=2.7Hz)	**C-5**	123.32
--	**--**	**C-6**	141.13
H-7	8.00,7.98 (1H,dd,*J*=9,2.7Hz)	**C-7**	121.23
H-8	7.42 (1H, d,*J*=9Hz)	**C-8**	117.21
--	**--**	**C-9**	159.38
--	**--**	**C-10**	118.99
--	**--**	**C-2'=C-2**	105.08
--	**--**	**C-3'**	051.99
H-4'	6.86(1H,d,*J*=9 Hz)	**C-4'**	126.19
H-5'	6.77 (1H, t, *J*=8.9Hz)	**C5'**	119.96
H-6'	7.10(1 H, t,*J*= 9Hz)	**C-6'**	127.95
H-7'	6.59 (1H,d,*J*= 9Hz)	**C-7'**	106.87
--	**--**	**C-8'**	146.20
--	**--**	**C-9'**	136.01
H-10'	1.20(3H,s)	**C-10'**	018.03
H-11'	1.28 (3H,s)	**C-11'**	019.99
H-1''	3.21(2H,sextet,*J*=7.5Hz)	**C-1''**	048.90
H-2''	1.52(2H,quintet,*J*=7.5Hz)	**C-2''**	029.40
H-3''	1.28(2H,sextet,*J*=7.5Hz)	**C-3''**	019.04
H-4''	0.83(3H, t, *J*=5Hz)	**C-4''**	014.03

3.1.2.9cAbsorbancespectroscopy of SP-9

Absorbancespectroscopy of SP-9 was carried out to study the thermochromic behavior of the spiropyrans and to analyze the change of absorbance peak with change in temperature. As the temperatureincreases with regular intervals, the absorbance increases, which confirm the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC) **(Scheme 3.12)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.12: Conversion of SP-9 from SP form to MC form

The absorbance versus wavelength spectrum of SP-9 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-9 is given in **figure 3.9.**

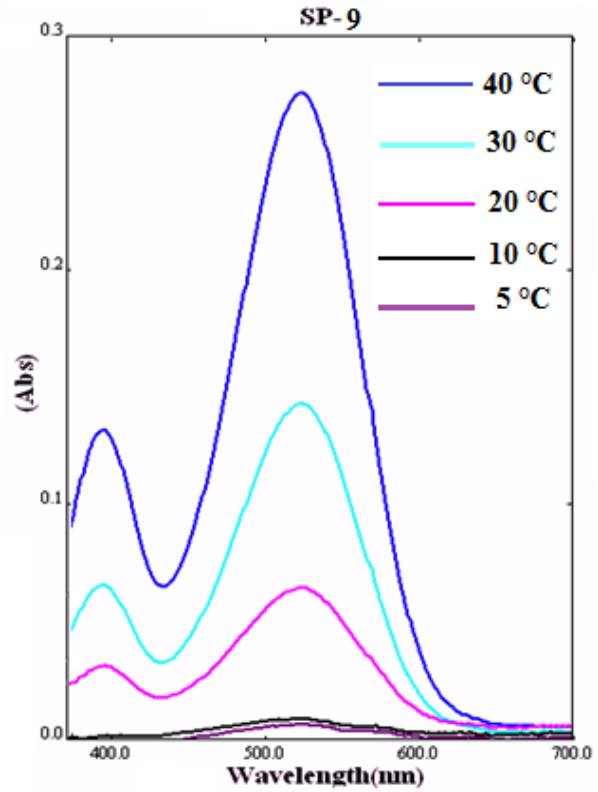


Figure 3.9: Absorbance versus wavelength spectrum of SP-9

3.1.2.10 Characterization of 1′,3′-dihydro-1′-(1-methylpropyl)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-10)

Physical constants of SP-10 are given in **table3.28**.

Table 3.28: Physical constants of SP-10

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-10	Citrine solid	0.57	80	190

* *n*-hexane: ethyl acetate (9:1)

3.1.2.10aSpectroscopic analysis of SP-10

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-10**is given in the **table 3.29**.

Table 3.29: IR data of SP-10

Code	$\bar{\upsilon}$ (cm^{-1})					
	sp^3C-H	Ar-H	C=C (Aliphatic)	C=C (Aromatic)	C-N	C-O
SP-10	2967, 2863	3072	1641	1610	1334	1211

3.1.2.10b^{1}H-NMR and ^{13}C-NMR analysis of SP-10

The formation of productis confirmedby the ^{1}H-NMR and ^{13}C-NMR analyses. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.00 ppm and 7.22 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 129.10 ppm and 122.09 ppm. The substitution was confirmed by the peak at 3.21 ppm for protons of –NC*H*– in ^{1}H-NMR and the peak at 49.90 ppm in ^{13}C-NMR.^{1}H-NMR and ^{13}C-NMR data is given in **table3.30**.

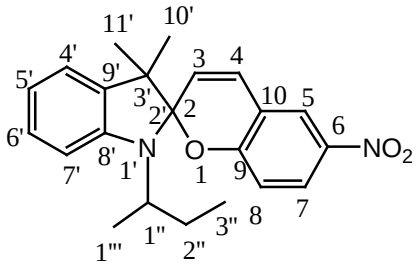


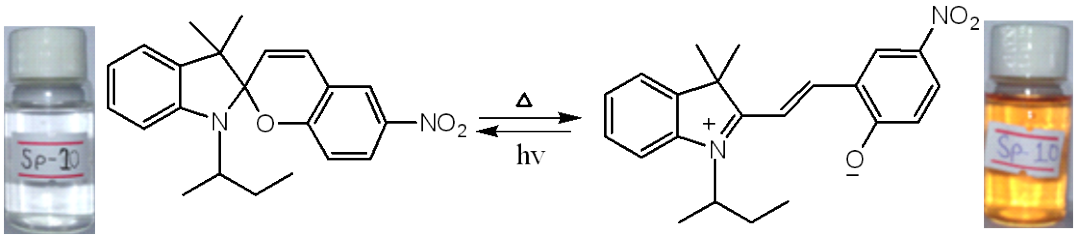
Table3.30: ^{1}H-NMR and ^{13}C-NMR of data SP-10

Proton	**δ(ppm),multiplicity and coupling constants*J*(Hz)**	**Carbons**	**δ(ppm)**
--	**--**	**C-2**	106.08
H-3	6.00 (1H,d,*J*=10.5Hz)	**C-3**	129.10
H-4	7.22(1H,d,*J*=10.5Hz)	**C-4**	122.09
H-5	8.23 (1H, d, *J*=3Hz)	**C-5**	123.31
--	**--**	**C-6**	141.03
H-7	8.01,7.98 (1H,dd,*J*=9,3Hz)	**C-7**	121.22
H-8	7.42(1H, d,*J*=9Hz)	**C-8**	117.01
--	**--**	**C-9**	159.38
--	**--**	**C-10**	119.12
--	**--**	**C-2'=C-2**	106.08
--		**C-3'**	052.70

H-4'	6.87(1H,d,*J*=9Hz)	**C-4'**	126.19
H-5'	6.81(1H, t, *J*=8.8Hz)	**C5'**	119.96
H-6'	7.08 (1H, t,*J*=8.9Hz)	**C-6'**	127.94
H-7'	6.57(1H,d,*J*=9Hz)	**C-7'**	106.87
--	**--**	**C-8'**	146.20
--	**--**	**C-9'**	135.40
H-10'	1.09(3H,s)	**C-10'**	017.40
H-11'	1.13 (3H,s)	**C-11'**	019.92
H-1''	2.79(1H,sextet,*J*=7.8Hz)	**C-1''**	049.90
H-2''	1.53(2H,quintet,*J*=7.5Hz)	**C-2''**	030.47
H-3''	0.85(3H,t,*J*=7.5Hz)	**C-3''**	014.04
H-1'''	1.25 (3H, d,*J*=7.5Hz)	**C-1'''**	021.03

3.1.2.10c Absorbancespectroscopy of SP-10

Thermochromic behavior of SP-10 was studied by using UV-Visible spectroscopy. This behavior of spiropyrans was analyzed by observing the change of absorbance peak with change in temperature. As the temperature increases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC)**Scheme 3.13**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.13: Conversion of SP-10 from SP form to MC form

The absorbance versus wavelength spectrum of SP-10 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-10 is given in **figure 3.10.**

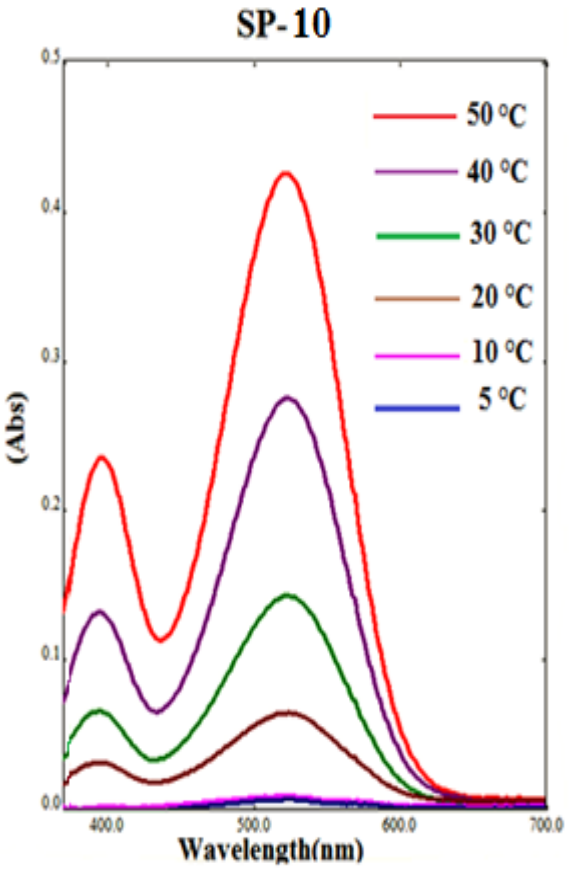


Figure 3.10: Absorbance versus wavelength spectrum of SP-9

3.1.2.11 Characterization of 1′,3′-dihydro-1′-(1-methylacetate)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-11)

PhysicalconstantsofSP-11aregivenin**table3.31**.

Table 3.31: Physical constants of SP-11

Code	**Physical Appearance**	**R_f*value**	**% Yield**	**M.P(°C)**
SP-11	Pink solid	0.42	70	147

* *n*-hexane: ethyl acetate (9:1)

3.1.2.11aSpectroscopic analysis of SP-1

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-11** is given in the **table 3.32**.

Table 3.32: IR data of SP-11

Code	$\bar{\upsilon}$ (cm^{-1})							
	sp^{3}C-H	**Ar-H**	**C=C (Aliphatic)**	**C=C (Aromatic)**	**C-N**	**C=O**	**C-O Ester**	**C-O Ether**
SP-11	2959, 2867	3074	1657	1612	1336	1742	1193	1210

3.1.2.11b^{1}H-NMR and ^{13}C-NMR analysis of SP-11

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 6.00 ppm and 7.20 ppm for two protons H-3 and H-4 respectively. In ^{13}C-NMR, these carbons (C-3 and C-4) appeared at 128.10 ppm and 122.31 ppm. The substitution was confirmed by the peak for methylene proton from N-substituted moiety–NCH_2(C=O)– appeared at 2.75 ppm. Other ^{13}C-NMR peak, however, was observed at52.07 ppm for the same carbon.^{1}H-NMR and ^{13}C-NMR data is given in **table3.33**.

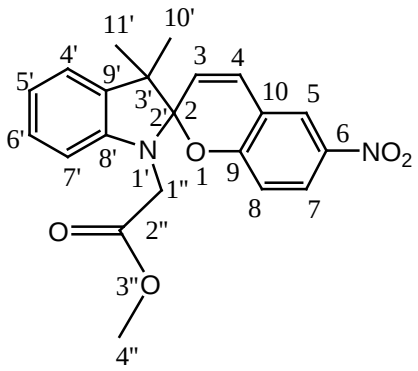


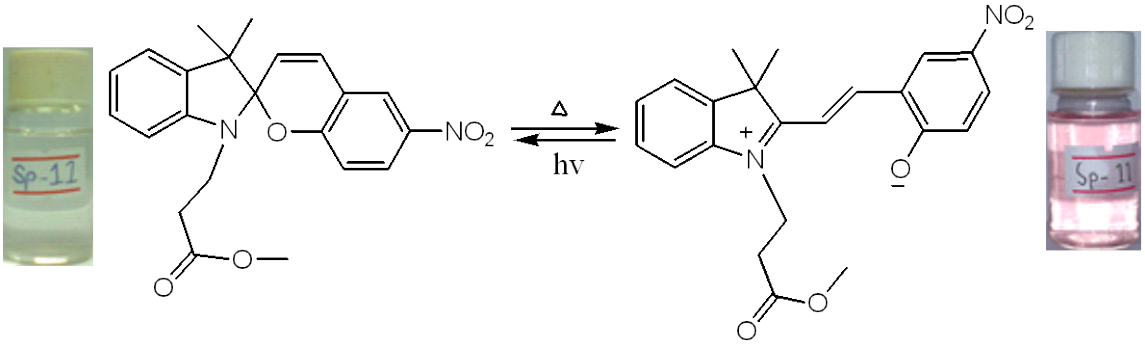
Table3.33: ^{1}H-NMR and ^{13}C-NMR data of SP-11

Proton	δ(ppm),multiplicity and coupling constants (*J*)Hz	Carbons	δ(ppm)
--	--	**C-2**	106.88
H-3	6.00 (1H, d, *J*=10.5Hz)	**C-3**	128.30
H-4	7.20 (1H, d, *J*=10.5Hz)	**C-4**	122.31
H-5	8.22 (1H, d, *J*=3Hz)	**C-5**	123.23
--	--	**C-6**	141.01
H-7	8.01,7.98 (1H, dd, *J*=9,3Hz)	**C-7**	122.11
H-8	7.11 (1H, d, *J*=8.7Hz)	**C-8**	115.82
--	--	**C-9**	159.70
--	--	**C-10**	119.22
--	--	**C-2'=C-2**	106.88
--	--	**C-3'**	044.98
H-4'	6.86 (1H, d, *J*=9Hz)	**C-4'**	123.31
H-5'	6.77 (1H, t, *J*=8.9Hz)	**C5'**	119.33
H-6'	7.10 (1H, t, *J*=9Hz)	**C-6'**	126.19
H-7'	6.60 (1H, d, *J*=9Hz)	**C-7'**	106.93
--	--	**C-8'**	147.28
--	--	**C-9'**	128.47
H-10'	1.19 (3H, s)	**C-10'**	019.98

H-11'	1.30 (3H, s)	**C-11'**	022.12
H-1''	2.75 (2H, s)	**C-1''**	052.07
--		**C-2''**	172.02
H-4''	1.08 (3H, t, *J*=7.5Hz)	**C-3''**	054.00

3.1.2.11c Absorbancespectroscopy of SP-11

Absorbancespectroscopy of SP-11 was carried out to study the thermochromic behavior of the spiropyrans and to analyze the change of absorbance peak with change in temperature. As the temperature increases with regular intervals, the absorbance increase,s which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC) **(Scheme 3.14)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.14: Conversion of SP-11 from SP form to MC form

The absorbance versus wavelength spectrum of SP-11 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-11 is given in **figure 3.11.**

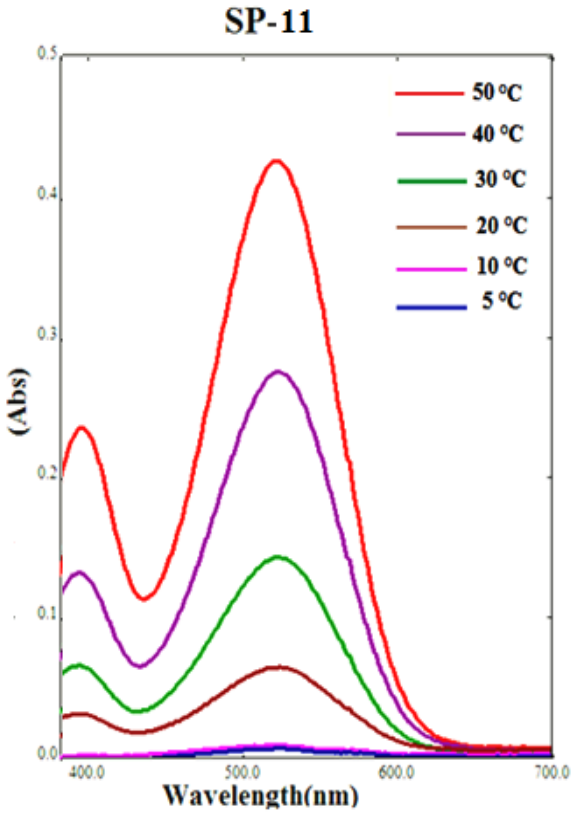


Figure 3.11: Absorbance versus wavelength spectrum of SP-11

3.1.2.12 Characterization of 1′,3′-dihydro-1′-(1-ethylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole](SP-12)

Physical constants of SP-11 are given in **table3.34**.

Table 3.34: Physical constants of SP-12

Code	Physical Appearance	R_f*value	% Yield	M.P(°C)
SP-1	Brown solid	0.53	81	165

* *n*-hexane: ethyl acetate (9:1)

3.1.2.12aSpectroscopic analysis of SP-12

The product was characterized byIR, ^{1}H-NMR and ^{13}C-NMR. In the IR spectrum, absorptions in the olefinic region indicated the synthesis of product. IR spectral data of the compound**SP-12**is given in the **table 3.35**.

Table 3.35: IR data of SP-12

Code	$\bar{\upsilon}$ (cm^{-1})							
	sp^3-H	Ar-H	C=C (Aliphatic)	C=C (Aromatic)	C-N	C=O	C-O Ester	C-O Ether
SP-12	2958, 2862	3075	1642	1606	1336	1746	1195	1213

3.1.2.12b ^{1}H-NMR and ^{13}C-NMR analysis of SP-12

^{1}H-NMR and ^{13}C-NMR analysis confirmed the formation of product. The characteristic peak of –CH=CH– in the ^{1}H-NMR spectrum appeared as two doublets at 5.92 ppm and 7.22 ppm for two protons. In ^{13}C-NMR, these carbons appeared at 129.10 ppm and 122.09 ppm. The substitution was confirmed by the peak at 4.03 for protons of –NCH_2CH_2– in ^{1}H-NMR and the peak at 44.66ppm in ^{13}C-NMR. ^{1}H-NMR and ^{13}C-NMR data is given in **table3.36**.

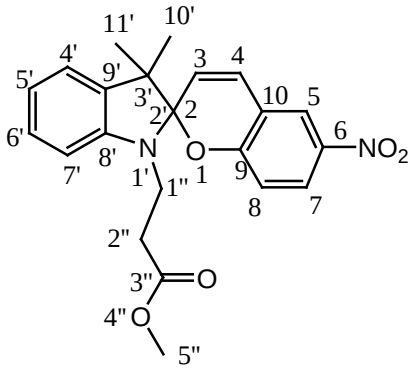


Table3.36: ^{1}H-NMR and ^{13}C-NMR data of SP-12

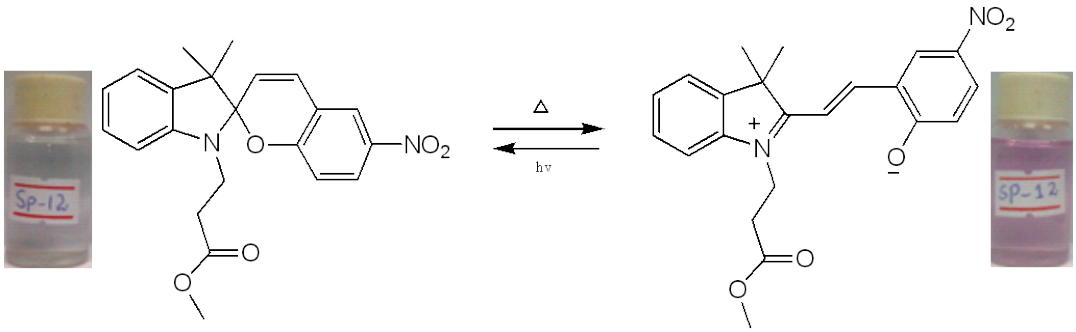
Proton	δ(ppm),multiplicity and coupling constants *J*(Hz)	Carbons	δ(ppm)
--	--	**C-2**	106.08
H-3	5.92(1H,d,*J*=10.5Hz)	**C-3**	129.10
H-4	7.22(1H,d,*J*=10.5Hz)	**C-4**	122.09

H-5	8.22 (1H,d,*J*=2.7Hz)	**C-5**	123.31
--	**--**	**C-6**	141.03
H-7	8.02,7.99 (1H,dd,*J*=9,2.7Hz)	**C-7**	121.22
H-8	6.87(1H,d, *J*=9Hz)	**C-8**	117.01
--	**--**	**C-9**	159.38
--	**--**	**C-10**	119.12
--	**--**	**C-2'=C-2**	106.08
--	**--**	**C-3'**	052.70
H-4'	6.81 (1H, d, *J*=8.8Hz)	**C-4'**	126.19
H-5'	6.57(1H,t,*J*=7.8Hz)	**C5'**	119.96
H-6'	7.13(1H,t,J=7.5Hz)	**C-6'**	127.94
H-7'	7.10(1H,d,*J*=7.5Hz)	**C-7'**	107.27
--	**--**	**C-8'**	146.25
--	**--**	**C-9'**	135.40
H-10'	1.09(3H,s)	**C-10'**	014.41
H-11'	1.13 (3H,s)	**C-11'**	019.93
H-1''	4.03(2H,t,*J*=6.9Hz),	**C-1''**	044.66
H-2''	4.00(2H,t,*J*=6.9Hz)	**C-2''**	026.47
--	**--**	**C-3''**	170.19
H-4''	1.22(3H,s)	**C-4''**	061.04

3.1.2.12cAbsorbancespectroscopy of SP-12

Thermochromic behavior of SP-12 was studied by using UV-Visible spectroscopy. This behavior of spiropyrans was analyzed by observing the

change of absorbance peak with change in temperature. As the temperature increases with regular intervals the absorbance increases, which confirms the conversion of colorless spirocyclic form (SP) to colored merocyanin form (MC)**(Scheme 3.15)**.



Colorless spirocyclic form (SP) Colored merocyanin form (MC)

Scheme 3.15: Conversion of SP-12 from SP form to MC form

The absorbance versus wavelength spectrum of SP-12 was taken in 1:1 ethanol water mixture. The absorbancespectrum of SP-12 is given in **figure 3.12.**

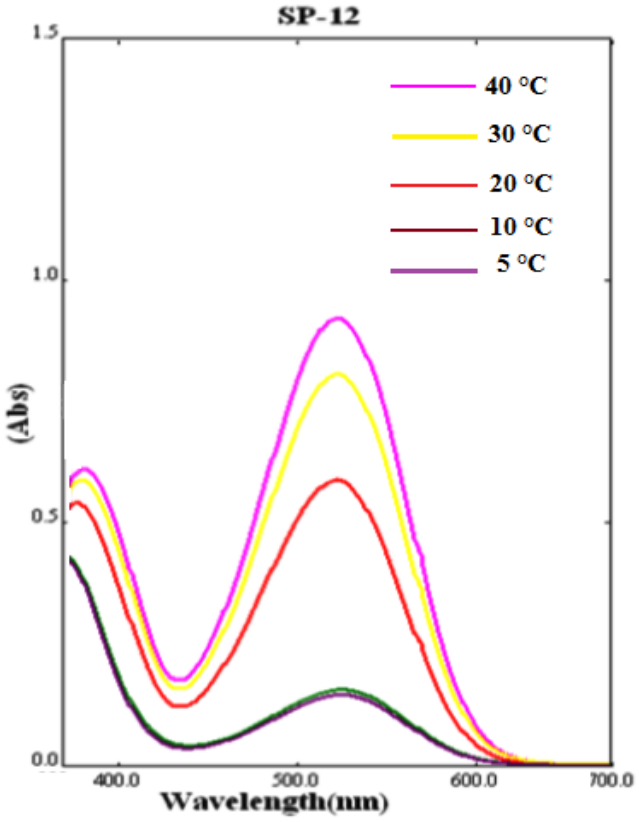
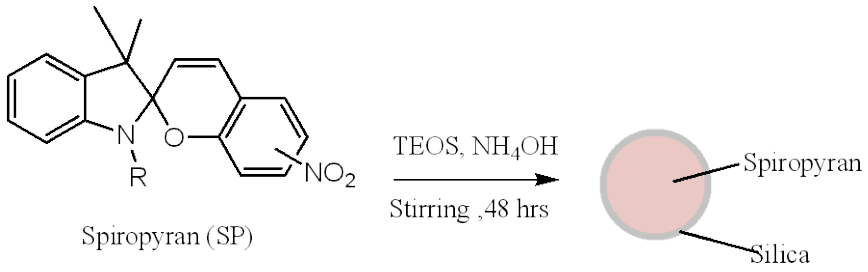


Figure 3.12: Absorbance versus wavelength spectrum of SP-12

The absorbance spectra were recorded from 5°C to 60°C.UV-Vis spectrum of all most all the spirpyrans shows an abrupt change from 10°Cto 20°C. These thermochromic dyes didn't show any regular change in its absorbance spectrum .This behavior confirms the discontinuous thermochromic nature of the spiropyrans dyes.

3.2 Encapsulation of Spiropyran

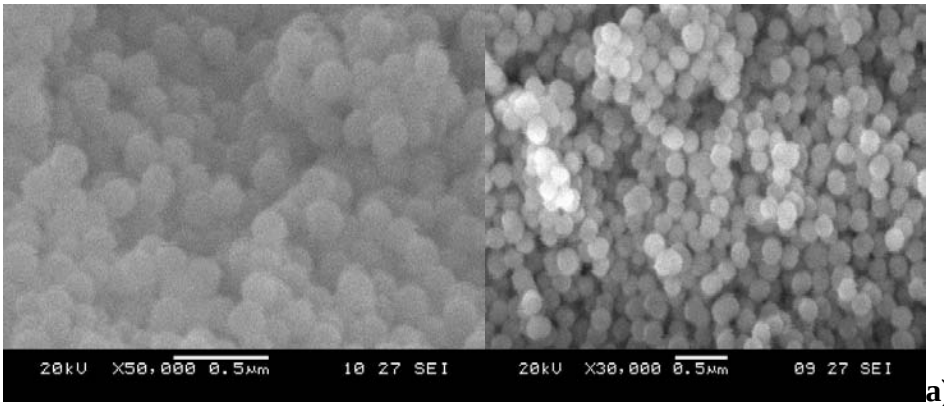
After the synthesis of spiropyran based thermochromic dye, it was encapsulated with in the silica matrix. Tetraethylorthosilicate was use as silica precursor. The reaction was carried out in basic medium as shown in **scheme 3.16.**



Scheme 3.16: Encapsulation of spiropyran in silica matrix

3.2.1Morphological study of encapsulated spiropyran

The morphological study of the encapsulated spiropyran dyes were carried out by Scanning Electron Microscopy (SEM). The SEM micrographs of the encapsulated dyes are shown in**Figure 3.14.** These micrographs indicates that the grain size in the range of 180-230nm. These are spherical and non-porous in nature. These appear as Separate grains.



a)

b)

Figure 3.14: SEM micrographs ofencapsulated spiropyran of a) SP-1 b) SP-2

3.2.3 Spectroscopic study of encapsulated spiropyran

The IR Spectroscopic analyses of the encapsulated spiropyrans were carried out. The chareteristic peak for Si-O-Si and Si-O-H bending vibrations appeared in all the IR spectra, which is in the range of 900-1460 cm^{-1} and O-H stretching vibration at average of 3200 cm^{-1}.

Spiropyrans have wide range of applications as mentioned earlier but the limitation of these thermochromicspiropyrans is that they are highly pH and moisture sensitive; because of this limitation these thermochromicspiropyrans can't be applied directly to open surfaces.

In order to overcome these limitations, these synthesizedthermochromicspiropyrans were encapsulated within the silica matrix. The silica encapsulations protects the thermochromicspiropyrans from the effect of pH and moisture but along with it also widens its applications to different media such as underground water temperature monitoring, aquatic temperature determination, protection of historical artifacts from the effect of changing climatic temperature.

Chapter 4
EXPERIMENTAL

4.1 Experimental Notes

All the reactions were carried out under anhydrous condition. An inert atmosphere was maintained under the static pressure of nitrogen gas using rubber septa and three way stopcock. All the apparatus was oven dried before use.

4.1.1 Substrate and Reagent

Dry and freshly distilled organic solvents were used.

a) Diethyl ether

Diethyl ether was dried by refluxing with Na/ benzophenone for two hours, distilled and stored under nitrogen.

b) Methanol

Methanol was dried by refluxing with magnesium turnings and few crystals of iodine. After about five hours when the yellowish color due to iodine disappeared and white precipitates were formed. Methanol was distilled under nitrogen at 65 $^{\circ}$C and stored under nitrogen atmosphere.

c) Acetonitrile

Acetonitrile was dried by refluxing with calcium hydride for 12 hrs and distilled under nitrogen at 82 $^{\circ}$C and it was also stored under nitrogen atmosphere.

4.1.2 Chromatography

Reactions were monitored by thin layer chromatography using precoated silica gel aluminium packed plates, Kiesal 60 HF_{254} from Merck (Germany). TLC was performed in ethyl acetate and *n*-hexane. For spot detection on TLC ultraviolet light (λ_{max} 254 and 365 nm) and locating agent ninhydrin was used.

4.1.3 Instrumentation

The compounds were characterized by their physical constants and spectro-analytical techniques. Melting points of synthesized compounds were recorded in open capillaries using Gallenkamp melting point apparatus (MP-D) and were uncorrected. The IR spectra were recorded on Thermo Scientific Nicolet 6700. ^{1}H-NMR and ^{13}C-NMR

spectra were recorded on Bruker AV-300 MHz spectrometer using desired solvent as indirect reference. UV/Vis spectroscopy was carried out at different temperatures using Schimadzu spectrophotometer, model Pharmaspec UV-1700. Surface morphological studies were performed by SEM (JEOI, JSM-5910), operating at 20 KV with different magnification power.

4.2 General Procedure for Synthesis of Substituted Indole

0.795g (5mmoles) of 2,3,3-trimethyl-3*H*-indole was dissolved in dry distilled acetonitrile (15mL), 2.18g (20mmoles) of alkyl halide was added to the reaction mixture. The reaction was allowed to reflux for 78 hours and was monitored by TLC, till the completion of reaction. Cooled to the room temperature and concentrated under reduced pressure. The residue was added to n-hexane (15ml) and dispersed well by ultra-sonication. The insoluble solid was recovered by filtration. The solid and KOH (4.0 mmol) were added to water and stirred at room temperature for 10 min. The solution was extracted with diethyl ether, washed with distilled water, brine, dried over anhydrous Na_2SO_4 and the excess solvent was removed under reduced pressure.

4.2.1 Synthesis of 1-ethyl-3,3-dimethyl-2-methyleneindoline (TH-1)

The compound (TH-1) was synthesized by the same general procedure as given above, using 2,3,3-trimethyl-3*H*-indol (0.795g, 5mmole), dry distilled acetonitrile (15mL), ethyl bromide (2.18g, 20mmoles) and KOH (4.0 mmoles).

Light orange liquid was obtained with yield of 80%. TH-1 was used without further purification in the next step.

4.2.2 Synthesis of 3,3-dimethyl-2-methylene-1-propylindoline (TH-2)

The compound (TH-2) was synthesized by the same general procedure as given before, using 2,3,3-trimethyl-3*H*-indol (0.795g,5mmole), dry distilled acetonitrile (15mL), propyl bromide (1.623g, 10mmoles) and KOH (4.0 mmoles).

Dark pink oily product was obtained with yield of 79%. This product was used in next step without further purification.

4.2.3 Synthesis of 1-Butyl-3,3-dimethyl-2-methyleneindoline (TH-3)

The compound (TH-3) was synthesized by the same general procedure as given before, using 2,3,3-trimethyl-3*H*-indol (0.795g, 5mmole),dry distilled acetonitrile (15mL), n-butyl bromide (2.055g, 15mmoles) and KOH (4.0 mmoles)..

Yellow oily product was obtained with yield of 86%. This product was used in next step without further purification.

4.2.4 Synthesis of 1-sec-butyl-3,3-dimethyl-2-methyleneindoline (TH-4)

The compound (TH-4) was synthesized by the same general procedure as given before, using 2,3,3-trimethyl-3*H*-indol (0.795g, 5mmole), dry distilled acetonitrile (15mL), isobutyl bromide (3.95g, 28.8mmoles) and KOH (4.0 mmoles).

Pink oily product was obtained with yield of 95%. This product was used in next step without further purification.

4.2.5 Synthesis of methyl-2-(3,3-dimethyl-2-methyleneindolin-1-yl)acetate (TH-5)

The compound (TH-5) was synthesized by the same general procedure as given before, using 2,3,3-trimethyl-3*H*-indol (0.159g, 1mmoles), dry distilled acetonitrile (15mL), methyl bromo acetate (0.832g, 2.16mmoles) and KOH (4.0 mmoles).

Blackish brown oily product was obtained with yield of 72%. This product was used in next step without further purification.

4.2.6 Synthesis of methyl-3-(3,3-dimethyl-2-methyleneindolin-1-yl)propanoate(TH-6)

The compound (TH-6) was synthesized by the same general procedure as given before, using 2,3,3-trimethyl-3*H*-indol (0.795g, 5mmole), dry distilled acetonitrile (15mL), ethyl bromo acatate (1.135g, 6.79mmoles) and KOH (4.0 mmoles).

Brawn oily product was obtained with yield of 91%. This product was used in next step without further purification.

4.3 General Procedure for Synthesis of Spiropyrans

Substituted indole was dissolved in 15mL of dry, distilled ethanol under static nitrogen atmosphere. This was set to gentle reflux with stirring and substituted benzaldehyde was added. The reaction was allowed to reflux for 6 hours, stirred for 12 hours and was monitored by TLC, until the reaction was complete. The product was recovered by filtration, washed with ethanol and dried in vacuo.

4.3.1 Synthesis of 1′,3′-dihydro-3′,3′-dimethyl-1′-ethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-1)

The compound (SP-1) was synthesized by the same general procedure as given above, using 1-ethyl-3,3-dimethyl-2-methyleneindoline (TH-1) (0.325g, 1.73mmole), EtOH (15mL) and 2-hydroxy-4-nitrobenzaldehyde (0.300g, 1.79 mmoles).

Dark khaki solid was obtained with yield of 90%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1650 (C=C Aliphatic), 1609 (C=C Aromatic), 1332 (C–N), 1213 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 1.08 (t, 3H, 7.5Hz, –NCH$_2$C*H*$_3$), 1.08 (s, 3H, –CC*H*$_3$), 1.20 (s, 3H, –CC*H*$_3$), 3.16 (q, 2H, 7.2 Hz, –NC*H*$_2$CH$_3$), 6.00 (d, 1H, 10.5 Hz, –CC*H*CH) 6.60 (d, 1H, 8.5 Hz, Ar*H*), 6.77 (t, 1H, 8.7 Hz, Ar*H*), 6.86 (d, 1H, 9 Hz, Ar*H*), 7.11 (d, 1H, 8.4 Hz, Ar*H*), 7.11 (t, 1H,8.9 Hz, Ar*H*),7.20 (d, 1H, 10.5 Hz, –CHC*H*C), 7.98, 8.00 (dd, 1H, 2.7, 9 Hz, Ar*H*), 8.22 (d, 1H, 2.7 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.05, 19.97, 22.1, 45.05, 52.72, 106.88, 106.94, 115.85, 119.18, 119.34, 122.12, 122.31, 123.30, 126.19, 128.06, 128.51, 136.03, 140.86, 147.28, 159.70.

4.3.2 Synthesis of 1′,3′-dihydro-3′,3′-dimethyl-1′-propyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-2)

The compound (SP-2) was synthesized by the same general procedure as given before, using 3,3-dimethyl-2-methylene-1-propylindoline (TH-2) (0.404g, 2.0mmole), EtOH (15mL) and 2-hydroxy-4-nitrobenzaldehyde (0.207g, 1.23mmoles).

Ecru solid was obtained with yield of 92%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1648 (C=C Aliphatic), 1608 (C=C Aromatic), 1333 (C–N), 1209 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 0.84 (t, 3H, 7.2Hz, –CH$_2$C*H*$_3$), 1.10 (s, 3H, –CC*H*$_3$), 1.19 (s, 3H, –CC*H*$_3$), 1.60, (m, 2H, 7.5 Hz, –CH$_2$C*H*$_2$CH$_3$), 3.08 (t, 2H, 7.2 Hz, –NC*H*$_2$CH$_2$), 6.00 (d,

1H, 10.5 Hz, –CC*H*CH), 6.59 (d, 1H, 7.5 Hz, Ar*H*), 6.77 (t, 1H,7.5 Hz, Ar*H*), 6.86 (d, 1H, 9 Hz, Ar*H*), 7.11 (t, 1H, 8.9 Hz, Ar*H*), 7.06, 7.11 (dd, 1H, 6.6, 8.4 Hz, Ar*H*), 7.20 (d, 1H, 10.5Hz ,–CHC*H*C), 7.97,7.99 (dd, 1H, 2.7, 9 Hz, Ar*H*), 8.21 (d, 1H, 2.7 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO, TMS): δ (ppm) = 11.97, 19.97, 22.11, 26.32, 45.07, 52.72, 106.88, 106.94, 115.87, 119.18, 119.34, 122.12, 122.31, 123.30, 126.19, 128.06, 128.51, 136.03, 140.86, 147.28, 159.70.

4.3.3 Synthesis of 1′,3′-dihydro-3′,3′-dimethyl-1′-butyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-3)

The compound (SP-3) was synthesized by the same general procedure as given before, using 1-butyl-3,3-dimethyl-2-methyleneindoline (TH-3) (0.663g, 3.0mmole), EtOH (15mL) and 2-hydroxy-4-nitrobenzaldehyde (0.300g, 1.79mmoles).

Citrine solid was obtained with yield of 83%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1652 (C=C Aliphatic), 1608 (C=C Aromatic), 1325 (C–N), 1213 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 0.83 (t, 3H, 7.5Hz, $–CH_2CH_3$), 1.20 (s, 3H, –CCH_3), 1.24 (s, 3H, –CCH_3), 1.28 (sextet, 2H, 7.5 Hz, $–CH_2CH_2CH_3$), 1.52 (quintet, 2H, 7.5Hz, $–CH_2CH_2CH_2$), 3.21 (t, 2H, 7.5 Hz, $–NCH_2CH_2$), 6.00 (d, 1H, 10.5 Hz, –CC*H*CH), 6.59 (d, 1H, 9Hz, Ar*H*), 6.77 (t, 1H, 9 Hz, Ar*H*), 6.86 (d, 1H, 9 Hz, Ar*H*), 7.10 (t, 1H, 9 Hz, Ar*H*), 7.12 (d, 1H, 9 Hz, Ar*H*), 7.21 (d, 1H, 10.5 Hz, –CHC*H*C), 7.98, 8.00 (dd, 1H, 2.7, 9 Hz, Ar*H*), 8.22 (d, 1H, 2.7 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.03, 18.03, 19.04, 19.99, 29.40, 48.90, 51.99, 106.01, 106.87, 107.01, 115.87, 119.96, 122.12, 122.13, 126.19, 127.95, 128.06, 128.53, 136.01, 141.09, 146.20, 158.09.

4.3.4 Synthesis of 1′,3′-dihydro-1′-(1-methylpropyl)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-4)

The compound (SP-4) was synthesized by the same general procedure as given before, using 1-sec-butyl-3,3-dimethyl-2-methyleneindoline (TH-4) (0.54g, 2.5mmole), EtOH (15mL) and 2-hydroxy-4-nitrobenzaldehyde (0.300g, 1.79mmoles).

Dark golden rod solid was obtained with yield of 80%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1649 (C=C Aliphatic), 1611 (C=C Aromatic), 1335 (C–N), 1210 (C–O Cyclic Ether). **^{1}H-NMR**

(300MHz, DMSO): δ (ppm) = 0.85 (t, 3H, 7.5Hz, –CH_2CH_3), 1.09 (s, 3H, –CCH_3), 1.135 (s, 3H, –CCH_3), 1.25 (d, 3H, 7.4 Hz, –$CHCH_3$), 1.53 (quintet, 2H, 7.5Hz, –$CHCH_2CH_3$), 2.79 (sextet, 1H, 7.8 Hz, –$NCH(CH_2)(CH_3)$), 6.03 (d, 1H, 10.5 Hz, –CC*H*CH), 6.59 (d, 1H, 9 Hz, Ar*H*), 6.83 (t, 1H, 8.9 Hz, Ar*H*), 6.89 (d, 1H, 9 Hz, –Ar*H*), 7.10 (t, 1H, 9 Hz, Ar*H*), 7.25 (d, 1H, 10.5 Hz, –CHC*H*C), 8.03 (d, 1H, 3 Hz, Ar*H*), 8.11, 8.13 (dd, 1H, 3, 9 Hz, Ar*H*), 8.21 (d, 1H, 3 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.83, 19.98, 21.09, 22.11, 29.47, 49.83, 52.70, 106.08, 107.01, 115.87, 119.18, 119.43, 122.12, 122.13, 123.33, 127.01, 128.06, 128.53, 136.05, 141.09, 147.52, 159.63.

4.3.5 Synthesis of 1′,3′-dihydro-1′-(1-methylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-5)

The compound (SP-5) was synthesized by the same general procedure as given before, using methyl-2-(3,3-dimethyl-2-methyleneindolin-1-yl)acetate (TH-5) (0.332g, 1.43,mmole), EtOH (15mL) and 2-hydroxy-4-nitrobenzaldehyde (0.207g, 1.23mmoles).

Bright maroon solid was obtained with yield of 80%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1656 (C=C Aliphatic), 1740 (C=O Ether), 1607 (C=C Aromatic), 1332 (C–N), 1212 (C–O Cyclic Ether), 119 (C–O Ester). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 1.08 (t, 3H, 7.5 Hz, –OCH_3), 1.19 (s, 3H, –CCH_3), 1.30 (s, 3H, –CCH_3), 2.75 (s, 2H, –NCH_2C=O), 5.99 (d, 1H, 10.5 Hz, –CC*H*CH), 6.58 (d, 1H, 10.5 Hz, –CHC*H*C), 6.60 (d, 1H, 8.5 Hz, Ar*H*), 6.817 (d, 1H, 9 Hz, Ar*H*), 6.84 (t,1H, 8.7 Hz, Ar*H*), 7.09 (t, 1H, 8.9 Hz, Ar*H*), 7.15 (d, 1H, 8.6 Hz, Ar*H*), 8.03, 8.05 (dd, 1H, 2.7,9 Hz, Ar*H*), 8.12 (d, 1H, 2.7 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 19.97, 22.11, 52.07,52.72, 54.00, 106.88, 106.94, 115.87, 119.18, 119.34, 122.12, 122.31, 123.30, 126.19, 128.06, 128.51, 136.03, 140.86, 147.28, 159.70,172.02.

4.3.6 Synthesis of 1′,3′-dihydro-1′-(1-ethylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-6)

The compound (SP-6) was synthesized by the same general procedure as given before, using methyl-3-(3,3-dimethyl-2-methyleneindolin-1-yl)propanoate (TH-6)

(0.812g, 3.3mmole), EtOH (15mL) and 2-hydroxy-4-nitrobenzaldehyde (0.300g, 1.79mmoles).

Light Khaki solid was obtained with yield of 79%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1639 (C=C Aliphatic), 1746 (C=O Ester), 1605 (C=C Aromatic), 1336 (C–N), 1211 (C–O Cyclic Ether), 1194 (C–O Ester). **^{1}H-NMR** (300MHz, DMSO, TMS): δ (ppm) = 1.22 (s, 1H, –OC*H*$_3$), 1.09 (s, 3H, –CC*H*$_3$), 1.13 (s, 3H, –CC*H*$_3$), 1.48,1.59 (sextet, 2H, 7.8,7.5Hz, –CH$_2$C*H*$_2$C=O), 3.08 (t, 2H, 7.5 Hz, –NC*H*$_2$CH$_2$), 5.92 (d, 1H, 10.5 Hz, –CC*H*CH), 6.69 (d,1H, 7.5 Hz, Ar*H*), 6.81 (t, 1H, 7.8 Hz, Ar*H*), 6.86 (d, 1H ,9 Hz, Ar*H*), 7.08 (t, 1H, 7.5 Hz, Ar*H*), 7.22 (d, 1H, 10.5 Hz, –CHC*H*C), 7.42 (d, 1H, 7.2 Hz, Ar*H*), 7.99, 8.01, (dd, 1H, 2.7, 9 Hz, Ar*H*), 8.22 (d, 1H, 2.7 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.41, 19.93, 26.47, 44.67, 52.70, 61.03, 105.78, 107.27, 116.11, 119.12, 119.96, 121.22, 122.19, 123.34, 126.20, 127.96, 129.18, 135.60, 141.04, 146.25, 159.34, 170.17.

4.3.7 Synthesis of 1′,3′-dihydro-3′,3′-dimethyl-1′-ethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole (SP-7)

The compound (SP-7) was synthesized by the same general procedure as given before, using 1-ethyl-3,3-dimethyl-2-methyleneindoline (TH-1) (0.424g, 2.26mmole), EtOH (15mL) and 2-hydroxy-5-nitrobenzaldehyde (0.300g, 1.79mmoles).

Khaki solid was obtained with yield of 79%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1651 (C=C Aliphatic), 1610 (C=C Aromatic), 1332 (C–N), 1212 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 1.08 (t, 3H, 7.5Hz, –NCH$_2$C*H*$_3$), 1.08 (s, 3H, –CC*H*$_3$), 1.20 (s, 3H, –CC*H*$_3$), 3.16, (q, 2H, 7.2 Hz, –NC*H*$_2$CH$_3$), 6.00 (d, 1H, 10.5 Hz, –CC*H*CH), 6.60 (d, 1H, 9 Hz, Ar*H*), 6.776 (t, 1H, 8.9 Hz, Ar*H*), 6.86 (d, 1H, 9 Hz, Ar*H*), 7.10 (t, 1H, 9 Hz, Ar*H*), 7.11 (d, 1H, 8.7 Hz, Ar*H*), 7.20 (d, 1H, 10.5 Hz, –CHC*H*C), 7.98, 8.01 (dd, 1H, 3,9 Hz, Ar*H*), 8.22 (d, 1H, 3 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.77, 19.99, 22.31, 44.99, 45.03, 105.90, 106.94, 115.81, 119.21, 119.34, 122.11, 122.31, 123.25, 123.31, 126.19, 128.10, 128.48, 140.44, 147.31, 160.01.

4.3.8 Synthesis of 1′,3′-dihydro-3′,3′-dimethyl-1′-propyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-8)

The compound (SP-8) was synthesized by the same general procedure as given before, using 3,3-dimethyl-2-methylene-1-propylindoline (TH-2) (0.398g, 2.0mmole), EtOH (15mL) and 2-hydroxy-5-nitrobenzaldehyde (0.300g, 1.79mmoles).

Blue bell solid was obtained with yield of 88%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1649 (C=C Aliphatic), 1608 (C=C Aromatic), 1333 (C–N), 1209 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 0.84 (t, 3H, 7.2Hz, $–CH_2CH_3$) 1.10 (s, 3H, $–CCH_3$), 1.20 (s, 3H, $–CCH_3$),1.59, (m, 2H, 7.5 Hz, $–CH_2CH_2CH_3$), 3.08 (t, 2H, 7.5 Hz, $–NCH_2CH_2$), 6.00 (d, 1H, 10.5 Hz, –CCHCH), 6.60 (d, 1H, 8.1 Hz, ArH), 6.86 (d, 1H, 9 Hz, ArH), 6.77 (t, 1H, 7.2 Hz, ArH), 7.10 (t, 1H, 6 Hz, ArH), 7.11 (d, 1H, 8.7 Hz, ArH), 7.20 (d, 1H, 10.5 Hz ,–CHCHC), 7.98, 8.01 (dd, 1H, 3, 9 Hz, ArH), 8.221 (d, 1H, 3 Hz, ArH). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 11.97, 19.97, 22.11, 26.32, 45.07, 52.21, 106.88, 106.94, 115.87, 119.18, 119.34, 122.12, 122.31, 123.30, 123.30, 126.19, 128.06, 128.51, 140.86, 147.28, 159.69.

4.3.9 Synthesis of 1′,3′-dihydro-3′,3′-dimethyl-1′-butyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-9)

The compound (SP-9) was synthesized by the same general procedure as given before, using 1-butyl-3,3-dimethyl-2-methyleneindoline (TH-3) (0.663g, 3.0mmole), EtOH (15mL) and 2-hydroxy-5-nitrobenzaldehyde (0.300g, 1.79mmoles).

Coral pink solid was obtained with yield of 85%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1651 (C=C Aliphatic), 1609 (C=C Aromatic), 1333 (C–N), 1207 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 0.83 (t, 3H, 7.5Hz, $–CH_2CH_3$), 1.20 (s, 3H, $–CCH_3$), 1.24 (s, 3H, $–CCH_3$), 1.28 (sextet, 2H, 7.5 Hz, $–CH_2CH_2CH_3$), 1.52 (quintet, 2H, 7.5Hz, $–CH_2CH_2CH_2$), 3.21 (t, 2H, 7.5 Hz, $–NCH_2CH_2$), 6.00 (d, 1H, 10.5 Hz, –CCHCH), 6.59 (d, 1H, 9Hz, ArH), 6.77 (t, 1H, 8.9 Hz, ArH), 6.86 (d, 1H, 9 Hz,–ArH), 7.10 (t, 1H,9 Hz, ArH), 7.21 (d, 1H, 10.5 Hz, –CHCHC), 7.42 (d, 1H, 9 Hz, ArH), 7.98, 8.00 (dd, 1H, 2.7, 9 Hz, ArH), 8.22 (d, 1H, 2.7 Hz, ArH). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.03,

18.03, 19.04, 19.99, 29.40, 48.90, 51.99, 105.08, 106.87, 117.21, 118.99, 119.96, 121.23, 121.99, 123.32, 126.19, 127.95, 129.10, 136.01, 141.13, 146.20, 159.38.

4.3.10 Synthesis of 1′,3′-dihydro-1′-(1-methylpropyl)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-10)

The compound (SP-10) was synthesized by the same general procedure as given before, using 1-sec-butyl-3,3-dimethyl-2-methyleneindoline (TH-4) (0.540g, 2.5mmole), EtOH (15mL) and 2-hydroxy-5-nitrobenzaldehyde (0.300g, 1.79mmoles).

Citrine solid was obtained with yield of 80%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1641 (C=C Aliphatic), 1610 (C=C Aromatic), 1334 (C–N), 1211 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 0.85 (t, 3H, 7.5Hz, –CH_2CH_3), 1.09 (s, 3H, –CCH_3), 1.13 (s, 3H, –CCH_3), 1.25 (d, 3H, 7.5 Hz, –$CHCH_3$), 1.53 (quintet, 2H, 7.5 Hz, –$CHCH_2CH_3$), 2.79 (sextet, H, 7.8 Hz, –$NCH(CH_2)(CH_3)$), 6.00 (d, 1H, 10.5 Hz, –$CCHCH$), 6.57 (d, 1H, 9Hz, Ar*H*), 6.81 (t, 1H, 8.8 Hz, Ar*H*), 6.87 (d, 1H, 9 Hz, Ar*H*), 7.08 (t, 1H, 8.9 Hz, Ar*H*), 7.22 (d, 1H, 10.5 Hz, –$CHCHC$), 7.42 (d, 1H, 9 Hz, Ar*H*), 7.98, 8.01 (dd, 1H, 3, 9 Hz, Ar*H*), 8.23 (d, 1H, 3 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.04, 17.40, 19.92, 21.03, 30.47, 49.90, 52.70, 106.08, 106.87, 117.01, 119.12, 119.96, 122.09, 121.22, 123.32, 126.19, 127.94, 129.10, 135.40, 141.03, 146.20, 159.38.

4.3.11 Synthesis of 1′,3′-dihydro-1′-(1-methylacetate)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-11)

The compound (SP-11) was synthesized by the same general procedure as given before, using methyl-2-(3,3-dimethyl-2-methyleneindolin-1-yl)acetate (TH-5) (0.582g, 2.5mmole), EtOH (15mL) and 2-hydroxy-5-nitrobenzaldehyde (0.412g, 2.4mmoles).

Pink solid was obtained with yield of 70%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1657 (C=C Aliphatic),1742 (C=C Ester), 1612 (C=C Aromatic), 1336 (C–N), 1210 (C–O Cyclic Ether), 1193 (C–O Ester).**^{1}H-NMR** (300MHz, DMSO, TMS): δ (ppm) = 1.08 (t, 3H, 7.5Hz, –OCH_3), 1.19 (s, 3H, –CCH_3), 1.30 (s, 3H, –CCH_3), 2.75 (s, 2H, –$NCH_2C{=}O$), 6.00 (d, 1H, 10.5 Hz, –$CCHCH$), 6.60 (d, 1H, 9 Hz, Ar*H*), 6.77 (t, 1H, 8.9 Hz, Ar*H*), 6.86 (d, 1H, 9 Hz, Ar*H*), 7.10 (t, 1H, 9 Hz, Ar*H*), 7.11 (d, 1H, 8.7 Hz, Ar*H*), 7.20 (d, 1H,

10.5Hz, –CHC*H*C), 7.98, 8.01 (dd, 1H, 3, 9 Hz, Ar*H*), 8.22 (d, 1H, 3 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO, TMS): δ(ppm) = 19.98, 22.12, 44.98, 52.07, 54.00, 106.88, 106.93, 115.82, 119.22, 119.33, 122.11, 122.31, 123.23, 123.31, 126.19, 128.10, 128.47, 141.01, 147.28, 159.70, 172.02.

4.3.12 Synthesis of 1′,3′-dihydro-1′-(1-ethylacetate)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-12)

The compound (SP-12) was synthesized by the same general procedure as given before, using methyl-3-(3,3-dimethyl-2-methyleneindolin-1-yl)propanoate (TH-6) (0.747g, 3.0mmole), EtOH (15mL) and 2-hydroxy-5-nitrobenzaldehyde (0.300g, 1.79 mmoles).

Brown solid was obtained with yield of 81%. **IR** ($\bar{\upsilon}_{max}$, cm^{-1}) 1642 (C=C Aliphatic), 1606 (C=C Aromatic), 1336 (C–N), 1213 (C–O Cyclic Ether). **^{1}H-NMR** (300MHz, DMSO): δ (ppm) = 1.22 (s, 1H, –OCH_3), 1.09 (s, 3H, –CCH_3), 1.13 (s, 3H, –CCH_3), 4.00 (t, 2H, 6.9Hz, –CH_2CH_2C=O), 4.03 (t, 2H, 6.9 Hz, –NC$H_2$$CH_2$), 5.92 (d, 1H, 10.5 Hz, –CC*H*CH), 6.57 (t, 1H, 7.8 Hz, Ar*H*), 6.81 (d, 1H, 8.8 Hz, Ar*H*), 6.87 (d, 1H, 9 Hz, Ar*H*), 7.10 (d, 1H, 7.5 Hz, Ar*H*), 7.13 (t, 1H, 7.5 Hz, Ar*H*), 7.22 (d, 1H, 10.5 Hz, –CHC*H*C), 7.99, 8.02, (dd, 1H, 2.7, 9 Hz, Ar*H*), 8.22 (d, 1H, 2.7 Hz, Ar*H*). **^{13}C-NMR** (75 MHz, DMSO): δ (ppm) = 14.41, 19.93, 26.47, 44.66, 52.70, 61.04, 106.08, 107.27, 117.01, 119.12, 119.96, 121.22, 122.09, 123.31, 126.19, 127.94, 129.10, 135.40, 141.03, 146.25, 159.30, 170.19.

4.4 General Procedure for the Encapsulation of as Synthesized Spiropyrans

50 mmoles of the synthesized spiropyrans was dissolved in 5mL of ethanol (A). 4.6 ml of this solution (A) was added to 8:2 ethanol water mixture. This reaction was stirred for 20 min followed by the addition of 5 ml of tetraethyl orthosilicate and 1 ml of ammonium hydroxide. The reaction was stirred for 48 hours. The resultant was recovered by filtration, washed with ethanol and dried in vacuo.

4.4.1 Encapsulation of 1′,3′-dihydro-3′,3′-dimethyl-1′-ethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-1E)

The encapsulation of compound (SP-1) was carried out by the same general procedure given as above, using SP-1 (0.083g, 50mmole).

4.4.2 Encapsulation of 1′,3′-dihydro-3′,3′-dimethyl-1′-propyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-2E)

The encapsulation of compound (SP-2) was carried out by the same general procedure given as before, using SP-2 (0.086g, 50mmole).

4.4.3 Encapsulation of 1′,3′-dihydro-3′,3′-dimethyl-1′-butyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-3E)

The encapsulation of compound (SP-3) was carried out by the same general procedure as given before, using SP-3 (0.090g, 50mmole).

4.4.4 Encapsulation of 1′,3′-dihydro-1′-(1-methylpropyl)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-4E)

The encapsulation of compound (SP-4) was carried out by the same general procedure as given before, using SP-4 (0.090g, 50mmole).

4.4.5 Encapsulation of 1′,3′-dihydro-1′-(1-methylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-5E)

The encapsulation of compound (SP-5) was carried out by the same general procedure as given before, using SP-5 (0.096g, 50mmole).

4.4.6 Encapsulation of 1′,3′-dihydro-1′-(1-ethylacetate)-3′,3′-dimethyl-7-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-6E)

The encapsulation of compound (SP-6) was carried out by the same general procedure as given before, using SP-6 (0.097g, 50mmole).

4.4.7 Encapsulation of 1′,3′-dihydro-3′,3′-dimethyl-1′-ethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-7E)

The encapsulation of compound (SP-7) was carried out by the same general procedure as given before, using SP-7 (0.083g, 50mmole).

4.4.8 Encapsulation of 1′,3′-dihydro-3′,3′-dimethyl-1′-propyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-8E)

The encapsulation of compound (SP-8) was carried out by the same general procedure as given before, using SP-8 (0.086g, 50mmole).

4.4.9 Encapsulation of 1′,3′-dihydro-3′,3′-dimethyl-1′-butyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-9E)

The encapsulation of compound (SP-9) was carried out by the same general procedure given as before, using SP-9 (0.090g, 50mmole).

4.4.10 Encapsulation of 1′,3′-dihydro-1′-(1-methylpropyl)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-10E)

The encapsulation of compound (SP-10) was carried out by the same general procedure as given before, using SP-10 (0.090g, 50mmole).

4.4.11 Encapsulation of 1′,3′-dihydro-1′-(1-methylacetate)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-11E)

The encapsulation of compound (SP-11) was carried out by the same general procedure as given before, using SP-11 (0.096g, 50mmole).

4.4.12 Encapsulation of 1′,3′-dihydro-1′-(1-ethylacetate)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP-12E)

The encapsulation of compound (SP-12) was carried out by the same general procedure as given before, using SP-12 (0.097g, 50mmole).

CONCLUSION

The present work has led to the following conclusions:

- Indoles was substituted with different alkyl and ester moities by simple nucleophilic reaction.
- These indoles were then converted to 12 novel spiropyrans by condensation of methylene base with nitro substituted *o*-hydroxy aromatic aldehydes.
- All the synthesized spiropyrans were characterized by physical data, NMR and IR spectroscopy.
- These spiropyrans were encapsulated with in the nano spheres of slice by using tetraethylorthosilicate as silicaprecursor.
- Encapsulation of thermochromic dye was confirmed by the SEM and IR techniques.
- Thermochromic property of these spiropyrans is confirmed by the UV-Vis spectroscopy, as the temperature increases, a discontinuous change in the absorbance specta of spiropyrans was observed.

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