



AN EFFICIENT NANO-CATALYSED SYNTHESIS, CHARACTERIZATION & STUDY OF FLUORESCENCE PROPERTY OF SUBSTITUTED PYRAZOLE.

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Abstract:

An α,β -Unsaturated Aldehyde, as starting material, was prepared by Claisen-Schmidt condensation (by using Strong basic reagent). The prepared Substrate material Cinnamaldehyde treated with Hydrazine hydrate in the presence of ZnO nano-catalyst under Microwave assisted solvent-free conditions to afford the substituted Pyrazole. Our review has been followed green synthesis approach & compared the reactions brought under the normal conditions in room temperature & microwave assisted conditions. The compound feature a donor- π -conjugated acceptor fluorescent activity system, and the fluorescence emission wavelength was measured in methanol & emitting at blue light ($\lambda_{em} = 430-505$ nm). We plotted a graph of intensity of emitted light v/s Concentration of the Compound (μM). The linear sketch of the graph reveals that the fluorescent emission increases with increasing the Concentration of the Compound. The obtained substituted compound was characterized by FT-IR (Bruker) prior of the fluorescence test. The use of nano-catalyst was the purpose of serving green chemistry methodology as well as the compound obtained was more rich in quality followed by possessed high yield. We studied the compound having electron withdrawing group, by which electron transition take place resulted that it exhibited more fluorescence than the compound having electron donating group.

Key Words: Cinnamaldehyde; ZnO Nano-Catalyst; Microwave assisted Synthesis; 3-Phenyl-1H-Pyrazole; Fluorescence emission & Fluorimetry.

I. Introduction:

Today, Nano-materials are playing as an All-rounder in the field of Science & Technology. Green chemistry has keen attachment with the Nano-Science for various advantages pertaining to

the quality of the synthesized products, quantitative benefits, moment reactions & reduction of reagents which are required for the reaction. 3-Phenyl-1H-Pyrazole was synthesized from Cinnamaldehyde in solvent-free condition & the reaction is completed for a minute under microwave irradiation [i]. We reported the role of ZnO Nano-Catalyst in the formation of Substituted Pyrazole & found wonder results that the yield of the compound was increased about 40% compared to that of reactions carried under the absence of Nano-Catalyst. The Microwave assisted synthesis was the method, which retains our objective to follow the green chemistry & as well as moment end of the reaction. The Pyrazole substance was Characterized & confirmed by FT-IR (Bruker). Finally, the obtained the pure compound was tested for its applications. Our review planned to test it for the fluorescence activity & secured success that Pyrazoles can exhibit the fluorescent light emission in the range of 400-550nm by Fluorimetry. We reported the fluorescence of 3-Phenylpyrazole at different concentrations (μM) & recorded the Intensities of emission [ii-viii, x] (Table-1). The compound was diluted in the methanol.

II. Instruments Used:

Melting point was determined in open capillary tubes in Buchi B-540 melting point apparatus. The reaction was monitored by thin layer chromatography using silica gel glass plates. The reaction was visualized by short Ultraviolet lamp & isolated in iodine chamber. FT-IR spectrometer (Bruker) was used. Fluorimetry (400-550nm, methanol solvent reference) is used.

III. Experimental section:

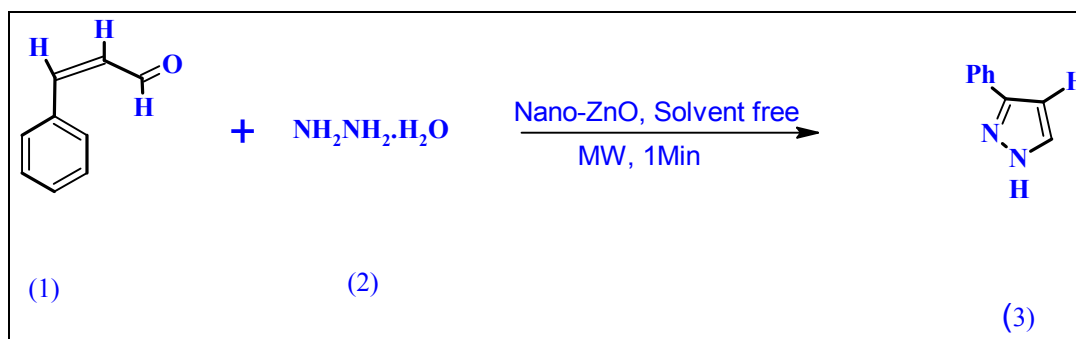
General Procedure for the Synthesis of 3-Phenyl-1H-Pyrazole:

To a solution of Cinnamaldehyde (0.01M), 0.5 g of Hydrazine hydrate (0.01M) was added & 2 equiv. of Nano-ZnO was mixed to the solution. The reaction mixture was kept under microwave oven for 1 Min. without solvents used. The reaction was monitored by TLC & iodine chamber. The spot at the product side was appeared. The crude compound along with Nano-ZnO powder was washed with very hot ethanol/water. The compound obtained was filtered, recrystallized by ethanol & finally dried.

3-Phenyl-1H-Pyrazole:

Yellow solid, m.p: 138°C , (% yield 90.00), IR (KBr): $\nu = 3343\text{ cm}^{-1}$ (-N-H stretch), 3052 cm^{-1} , 3013 cm^{-1} & 2927 cm^{-1} (aromatic C-H stretch & C=C stretch), 1284, 1344, 1384 & 1441 cm^{-1} (C-N stretch), 1583 cm^{-1} (aromatic C=C).

Synthesis



Analytical data-IR spectrum



Sample P-2.pdf

IV. Results & Discussion

Green Chemistry is a challenging task in the research because it is our duty to protect the environment from destruction. In earlier research, the usage of toxic chemicals results in release of toxic gases or liquids into the surrounding. We were projected to implement the green chemistry for being of eco-friendly. Microwave assisted solvent free synthesis follows the green chemistry. Nano-ZnO catalyst was yielded the product higher. After the product was formed, purification by ethanol was done & filtered & dried. The compound confirms by FT-IR , 3043 cm^{-1} for N-H stretch, 1284, 1344, 1384 & 1441 cm^{-1} (C-N stretch), 1583 cm^{-1} (aromatic C=C). The fluorescence property of the Compound (3) has been studied by Fluorimetry in methanol (400-550nm). The compound showed an extraordinary fluorescence emission depending on the concentration (μM) (see Tab-1). The electron donating Phenyl group substituted on Pyrazole will increase the intramolecular electron transfer and thus enhance the fluorescence of Pyrazole derivatives.

The broad range of fluorescence maxima and fluorescence quantum yields is attributed to varying contributions of charge transfer that are dependent on both the identity of the substituent. As a result, competitive excited-state proton/charge transfer properties have been observed in the pyrazoles studied, of which the spectral properties can be fine tuned by substituent. The Pyrazole (Fig-a) exhibited more Fluorescence intensity than the Pyrazole (Fig-b).

In the figure-a, the fluorescence emission enhances due to the electron transfer from ERG (Phenyl group), but the figure-b showed lower fluorescent emission due to less inductive effect of Carboxyl group [ix].

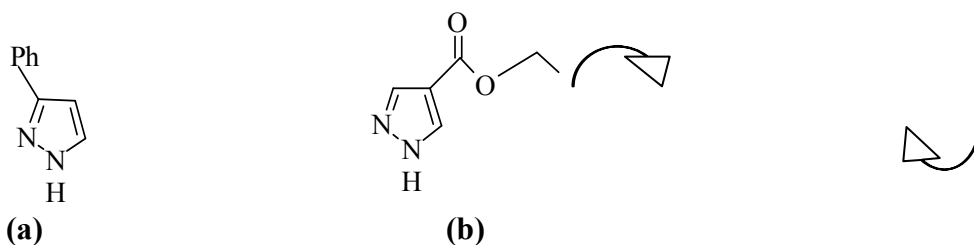
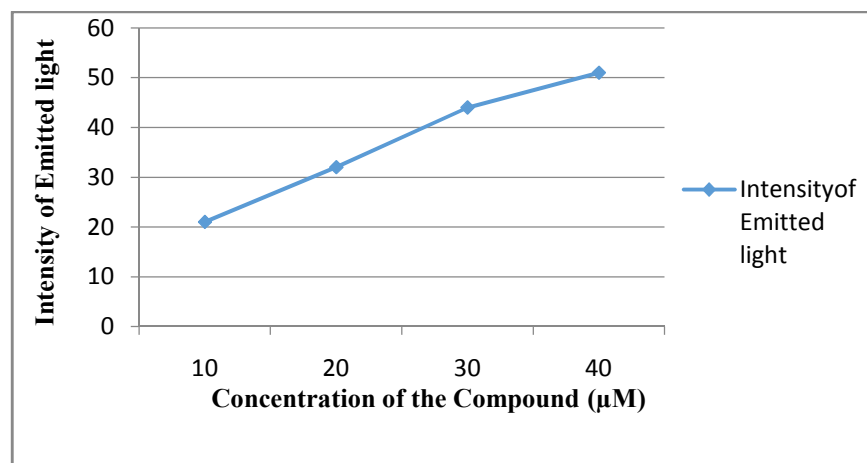


Fig-1: a) Pyrazole having Electron donating Phenyl group. b) Pyrazole having electron withdrawing carboxyl group.

The linear graph revealed that the intensity of the emitted light (y-axis) increases with increase in the concentration of the compound (x-axis) as shown in the Fig-2.

Fig-2: Concentration ((μ M) v/s Intensity of light**Table-1**

Concentration of the Compound (μ m)	Intensity of Emitted light
10	21
20	32
30	44
40	51
50	62
60	71

V. Conclusion:

We found that heterocyclic compounds have vast applications in various fields. The fluorescence property of this compound makes more advances in Optics & Electronics. The use of Nano-Catalyst results the higher quality of the products as well as higher quantity. Hence, Nano-Catalysts play as an all-rounder in science & technology.

The compound feature a donor- π -conjugated acceptor fluorescent activity system, and the fluorescence emission wavelength was measured in methanol & emitting at blue light ($\lambda_{em} = 430-505$ nm). We plotted a graph of intensity of emitted light v/s Concentration of the Compound (μ M). The linear sketch of the graph reveals that the fluorescent emission increases with increasing the Concentration of the Compound. The obtained substituted compound was characterized by FT-IR (Bruker) prior of the fluorescence test. The use of nano-catalyst was the purpose of serving green chemistry methodology as well as the compound obtained was more rich in quality followed by possessed high yield. We studied the compound having electron withdrawing group, by which electron transition take place resulted that it exhibited more fluorescence than the compound having electron donating group

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