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Synthesis and photochemical investigation of 1,2-di(pyrimidine-2-yl)diazine

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ABSTRACT

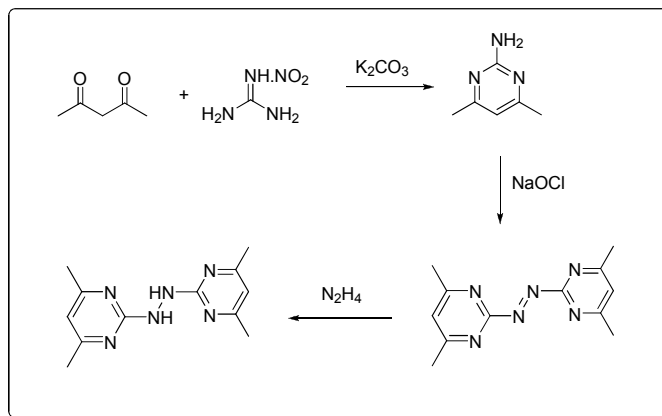
Pyrimidine is a prominent member of the diazine family of heterocycles and literature scanning revealed that it is found in nature as a component of nucleic acids nucleotides and corresponding nucleosides. The condensation reaction of a diketone and guanidine nitrate to form amine-functionalized pyrimidine and it was further oxidatively coupled with other unit to get the azo linked bis pyrimidine unit. Finally, it was further reduced with hydrazine to get titled compounds. The synthesized compounds were characterized by spectral techniques, viz. FT IR, ¹H NMR and ¹³C NMR spectra. UV-irradiation study of the 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine) showed a reversible isomerization of the compound.

Keywords: pyrimidine, diazine, photochemical, UV-irradiation.

INTRODUCTION

In the recent years, there has been considerable importance shown for the synthesis and characterization of conjugated organic compounds because of their wide range of applications for electronic and optoelectronic devices [1]. Fluorescent chromophores, which have planar and rigid π -conjugated systems, are of interest as functional materials in molecular probes [2]. Molecular fluorescence enables high sensitivity in detection, "ON OFF" switchability, subnanometer spatial resolution and submilli second temporal resolution [3]. The parent oligopyridines (2, 20-bipyridine, 2, 20: 60, 200-terpyridine and 1, 10-phenanthroline) possess extremely low fluorescence quantum yield and undesirable short emission wavelength. The introduction of electron donating groups leads to an enhancement in quantum yield and a shift to the visible region of the emission wavelength [4]. The suitably arranged ring nitrogen in 2,20:60,200-Terpyridine is known for its good coordination ability. The luminescent properties of Terpyridines upon coordination with metal ions are attractive for the technological applications such as light emitting devices and probes over a large spectral range [5]. Based on the large binding constants between the terpyridine ligand and various metal ions, the choice of ligand has a marked influence on the luminescence properties of the resulting supramolecular assemblies [6]. The conjugated 2,4,6-trisubstituted pyrimidine derivatives have shown important fluorescence properties [7], as well as self-assembly properties [8], and 2,4-diarylvinylpyrimidines have also been described as good fluorophores [9], pH sensors [10], and two-photon absorption chromophores [11]. Functionalization of pyrimidine with two 2-pyridyl groups in positions 2 and 4 leads to an effective tridentate ligand for metal cations (similar to a 2,20:60,200-terpyridine) that can generate various useful materials [12]. The additional nitrogen of the pyrimidine ring is providing a flat bridging acceptor ligand that leads to a large delocalized π surface; hence, the synthesis of new pyrimidine analogues of terpyridine is a good option to obtain high emission efficiency as well as new emission colors. Pyrimidine, which is a highly π -deficient aromatic heterocycle, can therefore be used as electron withdrawing part in push-pull structures for intramolecular charge transfer. The effect of different protic and aprotic solvents on the optical absorption and emission properties of 4-arylvinyl-2, 6-di (pyridin-2-yl)- pyrimidines were studied [13]. UV-visible spectroscopy is routinely used in the quantitative determination of solution of transition metal ions and highly conjugated organic compounds. Because of

its sensitivity, UV-visible spectroscopy has been particularly useful in identifying and analyzing foreign material in polymers. Copolymer composition also tends itself to itself to UV-visible analysis if one of the repeating units has the requisite chromophore. Hence, in this research paper, it is aimed at synthesizing the compounds (Scheme 1) of the type, 4,6-dimethylpyrimidine-2-amine (Compound I), 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine) (Compound II), 2,2'-hydrazine-1,2-diylbis (4,6-dimethylpyrimidine) (Compound III). It is also planned to characterize these compounds by IR, ^1H NMR and ^{13}C NMR spectral data. It is also aimed to study the photochemical studies of 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine) (Compound II).



Scheme 1

MATERIALS AND METHODS

The chemicals used in this work AnalaR grade. The solvents were purified following the standard procedures as reported in the literature. UV absorption of the solution measured on an Agilent 8453A UV-visible spectrophotometer.

Synthesis of 4,6-dimethylpyrimidine-2-amine

Guanidine nitrite (0.001428mmol) was dissolved with water (100mL) and the reaction mixture was stirred well at room temperature. The acetone (0.001428mmol) was added drop by drop followed by potassium carbonate (0.001449mmol) and stirred well for overnight. A white colour solid obtained was filtered and washed with the same filtrate to get pure compound of 4, 6-dimethylpyrimidine-2-amine. FT-IR spectral data (cm^{-1}): 3333(N-H), 2850 (C-H), 1238 (C-N), 1431(C=C); ^1H NMR Spectral data (δppm): 2.2 (3H, s, CH_3), 6.3 (1H, s, CH), 6.4 (2H, s, NH_2); ^{13}C NMR Spectral data(δppm):23 (s, CH_3), 167 (m, $\text{CH}_3\text{-C}$), 109 (m, CH), 163 (m, C- NH_2).

Synthesis of 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine)

4,6-dimethylpyrimidine-2-amine (0.0084mmol) was dissolved in 50mL of hypo solution (5%) and the reaction mixture was stirred well for 1h at room temperature. The colour of the solution turned red-brown along with solid and then it was filtered to get fairly pure compound of 2,2'-(Z)-diazene-1,2-diylbis(4,6-dimethylpyrimidine). ^1H NMR Spectral data (δppm): 2.3(3H, s, CH_3), 6.3 (1H, s, CH); ^{13}C NMR Spectral data (δppm):23 (s, CH_3), 167 (m, $\text{CH}_3\text{-C}$), 109 (m, CH), 130 (m, C-N=N).

Synthesis of 2,2'-hydrazine-1,2-diylbis(4,6-dimethylpyrimidine)

2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine) (0.0084mmol) is dissolved in minimum amount of ethanol and the reaction mixture was stirred well. The red colour solution is obtained. Then hydrazine hydrate (0.0390mmol) is added to the solution until the red colour was disappeared. The reaction mixture was stirred and heated to reflux for overnight. The reaction mixture was concentrated under reduced pressure, the white solid was obtained was filtered to get the compound, 2, 2-hydrazine-1,2-diylbis(4,6-dimethylpyrimidine). ^1H NMR Spectral data (δppm): 2.1(3H, s, CH_3), 8.9 (1H, s, CH); 6.3 (1H, s, NH); ^{13}C NMR Spectral data (δppm):23 (s, CH_3), 167 (m, $\text{CH}_3\text{-C}$), 109 (m, CH), 119 (m, C-N=N).

Photochemical study

Stock solution (500mM); in a 25mL volumetric flask, 0.0939g of probe was dissolved in acetonitrile and then diluted to the mark with acetonitrile. To a 50mL volumetric tube, 4.00mL of the solution was added and diluted to 50mL with methanol. The stock solution of metals (Ni, Na, Mg, Cd, Cu, Zn, Pb, Al) (5.00mM) in a 25mL volumetric flask, 10mg of anhydrous divalent metal salt was dissolved in water and then diluted to the mark with acetonitrile water mixture. Solubility of the polymers was determined in various solvents. 2-3mg of the compound was treated with 5mL of chloroform and kept aside for 6h with occasional shaking. 1.00mL of 500mM stock

solution and different concentration of metal solution to a 25mL volumetric tube, and then diluted to the mark with methanol, then the absorbance was recorded at 200-800nm. The photoisomerization /cyclization studies of all the polymers were carried out in steady state photolysis experiments using spectroline low-pressure mercury pencil ray lamp with a maximum output at 365nm. The intensity of the light reaching the matrix has been measured to be 3.01×10^{15} photons per second. The polymer was dissolved in chloroform solution in a 1cm quartz cuvette, irradiated for different intervals of time and then the UV absorption of the solution measured immediately. The experiment was repeated until completion effect of isomerization / cyclization or reduction in absorbance.

RESULTS AND DISCUSSION

In the present work, it has been synthesized 1,2-di(pyrimidin-2-yl)diazene segment using hypo solution and reacted with readily available 2-amino-4,6-dimethylpyrimidine to get the target compounds. The absorption spectral patterns of pyrimidine azo compound in chloroform solution upon irradiation with 360nm UV light as a function of time is shown in the following figure (Figure 1).

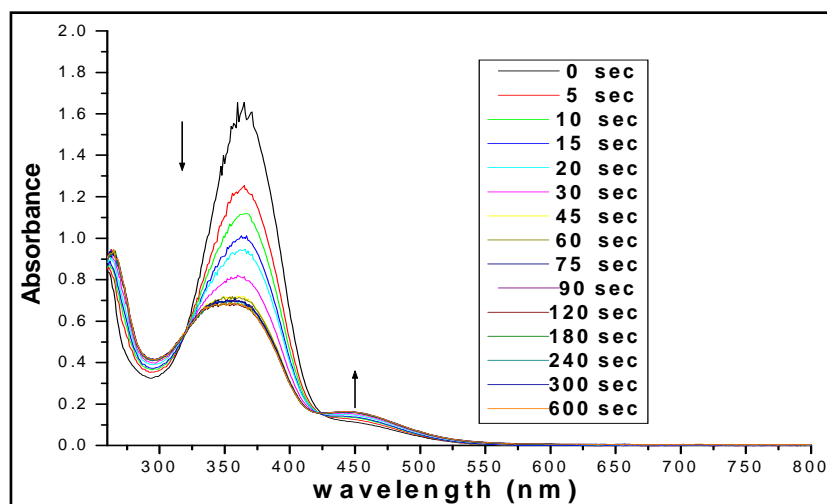


Figure 1: UV irradiation studies of 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine)

Before irradiation, the compound shows strong absorption band in the range of 350nm corresponds to the strong symmetry allowed $\pi-\pi^*$ electronic transition and the small absorption band in the range of 450nm corresponds to the weak symmetry forbidden $n-\pi^*$ transition of the *trans*-configuration of azobenzene units. The chloroform solution was irradiated with 360nm UV light; the intensity of the bands at 360nm slowly diminishes with increase at 450nm. After suitable UV irradiation period, a photostationary state was attained where the *cis*-isomer predominates. Such spectral changes clearly testify the *trans-cis* isomerization of azobenzene unit in all the polymers under UV light action. During the isomerization, the compound demonstrates the isobestic points at 425nm. It indicates that the two isomeric forms namely *trans* and *cis* azobenzenes only involved in the reversible photoisomerization reactions. The time required to attain the photostationary state for the compound in solution is around 300 seconds. The *cis*-fraction of the compound in the photostationary state is 0.31. In the photostationary state, the compound has very less amount of *cis*-fraction. It suggests that the methyl group attached to the opposite side of the azo group supplied enough electrons. Because of this push effect, the *trans-cis* isomerization reaction of the azobenzene unit is highly hindered under UV light action. After attaining the photostationary state, the resultant solution of the compound was placed in the dark environment; the absorption band in the range of 350nm was regained (up to 93-95% of the initial value) slowly due to the slow thermal *cis-trans* back isomerization of azobenzene unit at ambient temperature in dark. In another experiment, after attaining the photostationary state, the resulted solution was irradiated with 560nm visible light causes the *cis-trans* back isomerization very rapidly compared to that at ambient temperature in dark. The time required to recover the original state (around 95%) upon irradiation with 560nm visible light.

CONCLUSION

In the present work, the synthesis of the compounds containing pyrimidine moiety with azo linking group, viz., 4,6-dimethyl pyrimidine-2-amine, 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine), 2,2'-hydrazine-1,2-diylbis (4,6-dimethyl pyrimidine). All the synthesized compounds were characterized and assigned their structures by spectral techniques, viz. FTIR, ^1H NMR and ^{13}C NMR spectra. UV-irradiation study of the 2,2'-(Z)-diazene-1,2-diylbis-(4,6-dimethylpyrimidine) showed a reversible isomerization of the compound. The isomerization time and

yield were less when compared to that of azobenzene, which may be due to the electron rich nitrogen of pyrimidine moiety near to azo group.

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