

Synthesis and Characterization of New Azastilbenes-Oxindole Conjugated Chromophoric Frameworks

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Abstract: *We herein report the synthesis of conjugated chromophoric molecule possessing aza stilbenes and oxindole frameworks under catalyst-free condition by the reaction of 4-amino benzene sulfonic acid with isatin, 5-Bromo Isatin and 5-Iodo Isatin. All the newly synthesized compounds were well characterized by using different spectroscopic techniques like FT-IR spectroscopy, NMR spectroscopy. The developed method was found to be efficient, which have tolerated halogen functional groups. Furthermore the developed method afforded pure compounds just by a filtration process by skipping aqueous work-up extraction and column chromatography purification steps. The synthesized new azastilbenes-oxindole conjugated chromophoric frameworks possesses diverse functionality which might be useful for further chemical transformations to prepare a variety of libraries of derivatives desirable for a variety of applications..*

Keywords: 4-Amino benzene sulfonic acid, Azastilbenes, Chromophore, Isatin, Push-Pull, Oxindole

I. INTRODUCTION

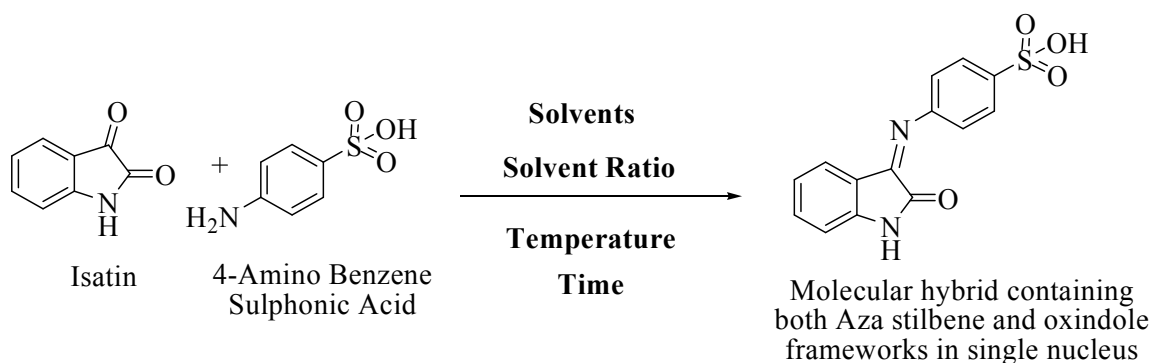
Azastilbenes are organic materials have been attracted a great deal of interest in various electronic and photonic applications such as semiconductor lasers [1], fluorescence sensors [2], fluorescent technology [3], nonlinear optics [4], organic light-emitting diodes [5] and optoelectronic devices [6], [7]. One of the advantages of the organic solid-state fluorescence materials is the ability to tune and control of fluorescence colors. In these contexts, different review articles which have recently published in the conjugated fluorescent chromophoric framework are given here [8]-[12]. Many extensive studies have shown that organic materials exhibit a variety of fluorescent colors in the solid state such as triphenylamine styryl dye [13], 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl]anthracene derivatives [14] and diphenylamino-carbazole pyridinium dyes [15]. From these studies, it indicated that pi-conjugated system influences the photonic properties of the compounds. Recently, Nawong B. *et. al* [16] have reported a new simple push-pull azastilbene fluorophore (D- π -A system) exhibiting multi-color fluorescence by introducing electron-donating group (EDG) on ring A and electron-withdrawing group (EWG) on ring B of azastilbene skeleton. These types of compounds which comprise the pi-conjugated system in their molecules exhibit interesting electronic and photonic properties [17]-[20]. In addition to this, the work published by Fukunishi [21] showed the effect of substituents on the photonic properties of the compounds.

Owing to the prevalence and prominence of natural and synthetic Aza stilbene frameworks, synthetic chemists have attracted towards development of new methods for the synthesis of these molecules. Among the different reactions, the condensation reaction of activated amines with carbonyl compounds has been used commonly for the effective synthesis of Aza stilbene derivatives. With the advancement in the field of catalysis, a large number of strategies for the synthesis of a diverse range of Aza stilbene have been developed. Generally substituted amines are condensed with activated aldehydes or ketones in the presence of various basic catalysts. The detailed structure-activity relationship studies on the Aza stilbene framework have shown that the photonic properties of the compounds known to vary with the substituent pattern on both the rings. In this context, we envision the substituted azastilbene molecular scaffold which assimilates azastilbene as well as oxindole framework which might integrate properties of both, and the synergism of both the heterocyclic moieties in a single nucleus may result in the formation of some worthwhile

molecules. Despite the prominence of aza stilbenes as well as oxindole framework, there was no report yet in the literature on the synthesis of conjugated chromophoric scaffold containing azastilbene and oxindole framework in single nucleus. In this context, we propose the synthesis of new azastilbenes based push-pull conjugated chromophoric framework containing oxindole moiety.

II. RESULTS AND DISCUSSIONS

To optimize the reaction condition for efficient synthesis of molecular scaffold possessing also stilbenes and oxindole framework in single nucleus, In the beginning, we have tested the reaction of Isatin with 4-amino sulfonic acid in water at room temperature (Scheme 1). We have stirred the reaction for 24 hr under this reaction, but the desired product formation was not obtained (Entry 1, Table 1). The same reaction was then tried at higher temperature also which showed the formation of desired product (Entry 2,3, Table 1). Then we tried different solvents like Ethanol and methanol in this reaction, which also showed the promising results (Entry 4,5, Table 1). Next we explored the equal mixtures of solvents in this reaction at different temperature, which showed the increase in yield (Entry 6-9, Table 1). We observe the good yield of desired product with Water: MeOH solvent system (Entry 9, Table 1). Hence Further to increase the yield of this reaction, we tried different proportions of the solvents like Water: MeOH, 2:1, 3:1, 4:1 and observed the effect on yield (Entry 10-12, Table 1). The result showed that, the best yield can be obtained with Water: MeOH, 3:1 solvent system for 12 hr reflux. This same system was also explored at room temperature, but the result was not good (Entry 13, Table 1). Furthermore the same Water: MeOH, 3:1 solvent system under reflux was tested in reaction for different time like 6hr, 3 hr, 2 hr (Entry 14-16, Table 1) in which 3hr reaction time was sufficient to get a very good yield of the desired product (Entry 15, Table 1) which was ultimately selected as an optimized reaction condition for this reaction.



Scheme I: Optimization of Reaction Condition

Table I: Optimization of Reaction Condition^a

Entry	Solvents	Solvent Ratio	Temp	Time in hr	Yield
1.	Water	-	RT	24	-
2.	Water	-	60°C	24	24%
3.	Water	-	Reflux	24	42%
4.	EtOH	-	Reflux	24	52%
5.	MeOH	-	Reflux	24	32%
6.	Water: EtOH	1:1	RT	24	44%
7.	Water: EtOH	1:1	Reflux	24	65%
8.	Water: MeOH	1:1	RT	24	52%
9.	Water: MeOH	1:1	Reflux	24	71%
10.	Water: MeOH	2:1	Reflux	12	77%
11.	Water: MeOH	3:1	Reflux	12	94%

12.	Water: MeOH	4:1	Reflux	12	79%
13.	Water: MeOH	3:1	RT	12	44%
14.	Water: MeOH	3:1	Reflux	6	93%
15.	Water: MeOH	3:1	Reflux	3	92%
16.	Water: MeOH	3:1	Reflux	2	71%

^aReaction Condition: Isatin (1mmol) was reacted with 4-amino sulfonic acid(1mmol) in 10 ml Solvents.

III. EXPERIMENTAL

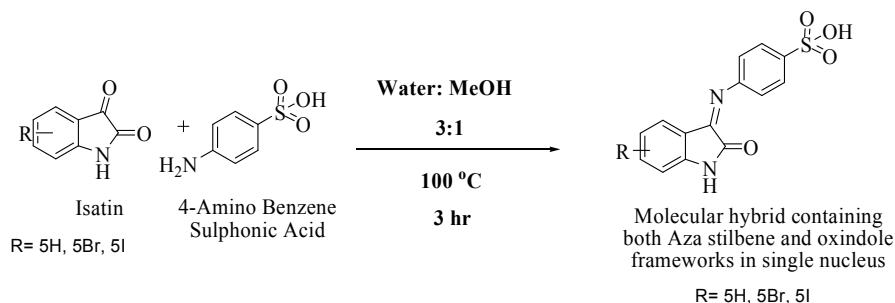
3.1 Materials

The reagents and solvents used in this work were obtained from commercial suppliers and used as it without additional purification. Chemicals compounds used in these reactions are Isatin, 5-Bromo Isatin, 5-Iodo Isatin, 4-amino Sulfonic acids were research grade quality. The solvent used were distilled water and Methanol was used as received without any further purification. The glasswares used in this study were made up of borosil glass. Heating methels were used for heating in this reaction. The compounds were dried under open air and IR Lamp.

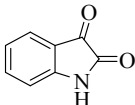
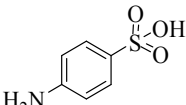
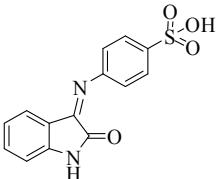
3.2 General Procedure

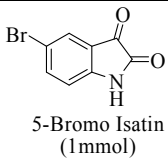
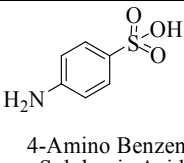
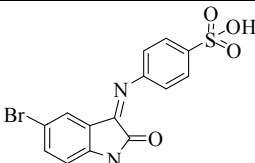
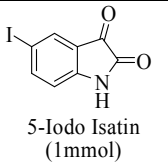
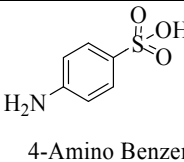
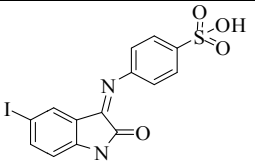
Isatin/5-Bromo Isatin/5-Iodo Isatin (1mmol) and 4-amino sulfonic acid (1mmol) was dissolved in 10 ml 3:1 water:MeOH solvent system and stirred at 100 °C. The reaction progress was continuously monitored through TLC. After 3 hr, the reaction was completed to give the desired product possessing aza stilbenes and oxindole framework in single nucleus as a precipitate. The thick precipitate of product was filtered and washed with distilled water. The precipitate was further purified by recrystallization in ethanol to afford the desired products.

3.3 General Scheme



3.4 Synthesized Compounds

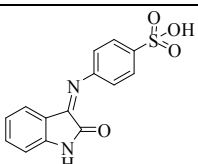
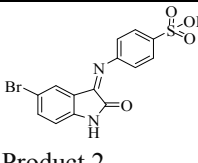
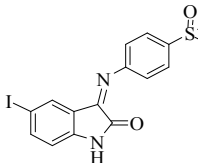
Reactant 1	Reactant 2	Reaction Conditions	Yield	Product
 Isatin (1mmol)	 4-Amino Benzene Sulphonic Acid (1mmol)	Water: MeOH (3:1), 100 °c, 3 hr	92 %	 Product 1

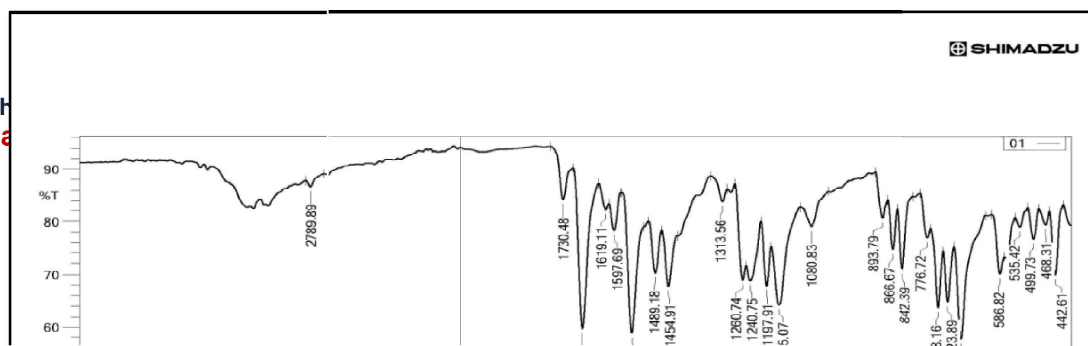
 5-Bromo Isatin (1mmol)	 4-Amino Benzene Sulphonic Acid (1mmol)	Water: MeOH (3:1), 100 °c, 3 hr	94 %	 Product 2
 5-Iodo Isatin (1mmol)	 4-Amino Benzene Sulphonic Acid (1mmol)	Water: MeOH (3:1), 100 °c, 3 hr	95 %	 Product 3

3.5 Characterization of Compounds

The synthesized compounds were submitted for spectral analysis using FT-IR and ¹H NMR Spectroscopy. The structure confirmation of the synthesized compounds was done by careful analysis of the obtained spectral data. The FT-IR spectrums of the synthesized compounds exhibited a key vibrational signal of C=N stretching at 1654-1671 cm⁻¹ along with other significant bands for corresponding functional groups (see Table II). The FT-IR Spectrum of Product 1 is shown in Fig. 1.

Table II: The FT-IR Data of the synthesized compounds in Cm⁻¹

Product	C=N	C=O	N-H	S=O	O-H	C-H
 Product 1	1666	1696	3195	1379	3440	3008
 Product 2	1671	1614	3098	1348	3397	2965
 Product 3	1654	1617	3155	1368	3403	2987



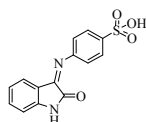
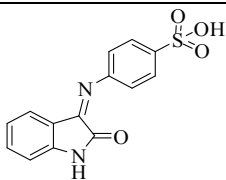
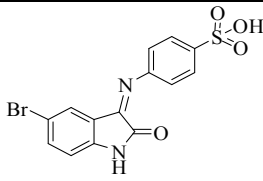
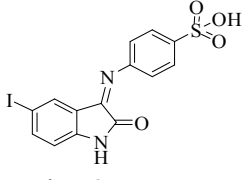


Figure 1: FT-IR Spectrum of Product 1

The ^1H NMR spectrum of the compound exhibited a singlet signal of an N-H proton 10.51-10.72 ppm responsible for a signal of N-H proton of isatin. ^1H NMR spectrum also showed other necessary peaks for aromatic protons. All this data confirm the formation of desired scaffold possessing aza stilbenes and oxindole framework (see Table III). The ^1H NMR Spectrum of Product 1 is shown in Fig. 2.

Table III: The ^1H NMR Data of the synthesized compounds in δ ppm

Product	Aromatic Proton	N-H Proton	O-H Proton
 Product 1	7.76 (<i>d</i> , 2H) 7.65 (<i>d</i> , 2H) 7.19 (<i>d</i> , 2H) 6.93 (<i>d</i> , 2H)	10.51 Broad Singlet	D ₂ O exchangeable
 Product 2	8.10 (<i>s</i> , 1H) 7.74 (<i>d</i> , 2H) 7.63 (<i>d</i> , 2H) 7.21 (<i>d</i> , 2H)	10.64 Broad Singlet	D ₂ O exchangeable
 Product 3	7.84 (<i>s</i> , 1H) 7.77 (<i>d</i> , 2H) 7.64 (<i>d</i> , 2H) 7.19 (<i>d</i> , 2H)	10.72 Broad Singlet	D ₂ O exchangeable

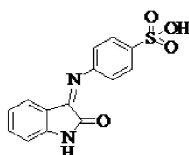


Figure 2: ^1H NMR Spectrum of Product 1

IV. CONCLUSION

We herein reported synthesis of new azastilbenes-oxindole conjugated chromophoric Frameworks in single nucleus. In this developed method, various Isatins electrophiles were allowed to react with nucleophilic 4-amino benzene sulfonic acids in 1:1 molar equivalence ratio under MeOH/H₂O (1:3) solvent system at 100 °C for 3 hr. This method has offered a quantitative yield of the desired scaffold possessing also Stevens and oxindole framework under catalyst-free condition. All the newly synthesized compounds were well characterized by using different techniques like FT-IR spectroscopy, NMR spectroscopy. The developed method was found to be efficient, which have tolerated different functional groups in this reaction. Furthermore the developed method afforded pure compounds just by a filtration process by skipping aqueous work-up extraction and column chromatography purification steps. These synthesized molecular frameworks containing aza stilbenes and oxindole moiety in single nucleus possess the diverse functionality which might be useful for further chemical transformations to prepare a library of derivatives desirable for a variety of applications.

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