



# Pigment Yellow 101 analogs from 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde – Synthesis and characterization



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## ABSTRACT

Pigment Yellow 101 analogs have been synthesized from 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde by combining with different aromatic diamines. Out of the four synthesized aldazines two show pigment properties and remaining show properties like dyes. Existence of excited state intramolecular proton transfer process between phenolic –OH and azomethine linkage (=N–) has been computationally ascertained. Two pigment analogs showed solid state fluorescent which were compared with commercially available Pigment Yellow 101. For dyes analogs, effects of solvent polarity on photophysical properties such as absorption, emission have been studied. Density functional theory and time dependent density functional theory computations have been used to investigate structural parameters and understanding photophysical properties of synthesized analogs. All these aldazines show good thermal stability.

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## 1. Introduction

The organic pigments as compared to the inorganic ones are brighter and have more intense color, while inorganic pigments exhibit better stability as compared to the organic pigments [1]. Organic pigments are more insoluble in most of the solvents than the organic dyes as the molecular lattices of organic pigments hold the molecules stronger together than the corresponding molecular lattices of dyes [2]. The first organic pigments [3,4] used commercially are all pure azo compounds with  $\beta$ -naphthol derivatives as coupling components. Production of pigments like C.I. Pigment Red 53:1 and C.I. Pigment Red 57:1 is the actual beginning of the era of organic pigments coloration [1,3,5,6]. Replacement of the naphthol based coupling component by acetaryl amide led to the first yellow azo pigments (eg Pigment Yellow 1).

2,2'-Dihydroxy-1,1'-naphthalazine also known as Pigment Yellow 101 is the first and only organic fluorescent yellow bis-azomethine pigment and commercially produced since 1899 [3,7]. Pigment Yellow 101 has brighter color and high photo stability. Due to its high photo stability, it is used as commercial

colorant for the coloration of viscose, in printing inks, artist's colors or non-destructive material testing [7–9,11]. Although Pigment Yellow 101 is known since 1899, its unique fluorescence property has been studied recently in experimentally and theoretically [12–15]. Time resolved spectroscopy [16] and ultrafast photo induced dynamic [13] study of Pigment Yellow 101 revealed that excited state intramolecular proton transfer (ESIPT) process occurred due to presence of –OH group on naphthalene ring nearby azomethine linkage. Theoretical support also provides to study fluorescence properties of it by using computational chemistry [14–17].

Considering the commercial importance of fluorescent organic pigments, we have synthesized analogs of Pigment Yellow 101. Instead of 2-hydroxynaphthalene-1-carbaldehyde we have used 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde **4**. This carbaldehyde was treated with hydrazine hydrate, 1,2-diaminobenzene, 1,3-diaminobenzene, 1,4-diaminobenzene to give different derivatives **6a–6d** and their photophysical properties and thermal stability have been studied. Density functional theory (DFT) and time dependent density functional theory (TD-DFT) are respectively used to confirm that the ESIPT process is feasible not in the phenolic –OH and nitrogen of the benzothiazole ring, but in the phenolic –OH group and azomethine linkage.

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## 2. Experimental

### 2.1. Materials and equipments

All the reagents and solvents were purchased from Sd Fine Chemicals Pvt Ltd and used without purification. All the solvents used were of spectroscopic grade. Melting point was recorded by open capillary on Sunder Industrial Product and is uncorrected. All the reactions are monitored by using pre-coated silica gel aluminum backed TLC plates; Kiesel gel 60 F<sub>254</sub> Merck (Germany). UV–Visible absorption measurements were carried out using a Spectronic Genesys 2 spectrophotometer with 1 cm length quartz cells. Fluorescence emission measurements were recorded on Cary Eclipse fluorescence spectrophotometer (Varian, Australia) using 1 cm length quartz cells. The FT–IR analysis was performed on a FTIR-8400S SHIMADZU spectrophotometer. Quantum yields of the compounds **6c** and **6d** were calculated using fluorescein ( $\Phi_{\text{fluorescein}} = 0.91$  in ethanol) [18] as a reference standard using the comparative method. <sup>1</sup>H NMR spectra were recorded on VXR 400-MHz instrument using TMS as an internal standard and DMSO as the solvent. Purification of all the compounds was generally achieved by recrystallization. The purity of compounds was generally ascertained by thin layer chromatography. The color coordinates of **6a** and **6b** were determined on CE-7000A Gretag-Macbeth computer color matching system. The color values were expressed by using CIE 1976 Color Space method. Thermo gravimetric analysis was carried out on a SDT Q600 TA Instruments. Method for thermo gravimetric analysis was done with ramp 10 °C per minute from ambient temperature to 600 °C under nitrogen atmosphere. Thermo gravimetric analyses (TGA) of analogs **6a–6d** are given in the supporting information.

### 2.2. Computational methods

The ground state (*S*<sub>0</sub>) geometry of the conformers and tautomers of the analogs **6a–6d** in their *C*<sub>1</sub> symmetry were optimized using the tight criteria in the gas phase as well as in the different solvents using DFT [19]. The vibrational frequencies at the optimized structures were computed using the B3LYP/6-31G(d) method to verify that the optimized structures correspond to local minima on the energy surface [20–22]. The vertical excitation energies at the ground-state equilibrium geometries were calculated with TD-DFT [23–26]. The low-lying first singlet excited state (*S*<sub>1</sub>) of each conformer was relaxed using the TD-DFT to obtain its minimum energy geometry. All the computations were carried out in vacuum and also in the solvents of different polarities using the Polarizable Continuum Model (PCM) [24,27]. All the electronic structure computations were carried out using the Gaussian 09 program [28]. The computed absorption spectra, emission wavelengths, oscillator strengths were studied using TD-DFT with PCM model on the basis of the optimized ground structures, emissions were calculated using TD-DFT from optimized structures in the excited state at B3LYP/6-31G(d) level of theory.

### 2.3. Synthesis

#### 2.3.1. Synthesis of 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde **4**

Carbaldehyde **4** was synthesized from 3-(1,3-benzothiazol-2-yl)naphthalen-2-ol [29] as previously reported [30].

#### 2.3.2. Synthesis of 1,1'-((1*E*,1'*E*)-hydrazine-1,2-diylidenebis(methanylylidene))bis(3-(benzo[d]thiazol-2-yl)naphthalen-2-ol) **6a**

A mixture of 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde (1.00 g, 3.3 mmol) and hydrazine hydrate (0.08 mL,

*d* = 1.02 gm L<sup>-1</sup>, 1.7 mmol) in ethanol was refluxed for 4 h. On cooling, a yellow pigment precipitate obtained was filtered and recrystallized by using methanol.

**Yield:** 64%; **M.p.** >300 °C.

**FT–IR (in cm<sup>-1</sup>):** 3211 (–OH stretch), 1623 (–C=N, imine), 1581 (–C=N, benzothiazole), 1453 (Aromatic ring), 1220 (C–O stretch), 754 (–C–S stretch).

Due to poor solubility NMR and HRMS could not be obtained.

#### **Elemental Analysis:**

**Calculated:** C, 71.27; H, 3.65; N, 9.23; S, 10.57.

**Found:** C, 71.25; H, 3.64; N, 9.21; S, 10.55.

#### 2.3.3. Synthesis of 1,1'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(3-(benzo[d]thiazol-2-yl)naphthalen-2-ol) **6b**

A mixture of 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde (1.00 g, 3.3 mmol) and 1,2-diaminobenzene (0.18 g, 1.7 mmol) in ethanol was refluxed for 4 h. On cooling, an orange pigment precipitate obtained was filtered and recrystallized by using methanol.

**Yield:** 68%; **M.p.** = 254–256 °C.

**FT–IR (in cm<sup>-1</sup>):** 3252 (–OH stretch), 1618 (–C=N, imine), 1585 (–C=N, benzothiazole), 1487 (Aromatic ring), 1283 (C–O stretch), 728 (–C–S stretch).

Due to poor solubility NMR and HRMS could not be obtained.

#### **Elemental Analysis:**

**Calculated:** C, 73.88; H, 3.84; N, 8.21; S, 9.39.

**Found:** C, 73.89; H, 3.83; N, 8.22; S, 9.38.

#### 2.3.4. Synthesis of 1,1'-((1*E*,1'*E*)-(1,4-phenylenebis(azanylylidene))bis(methanylylidene))bis(3-(benzo[d]thiazol-2-yl)naphthalen-2-ol) **6c**

A mixture of 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde (1.00 g, 3.3 mmol) and 1,4-diaminobenzene (0.18 g, 1.7 mmol) in ethanol was refluxed for 4 h. On cooling, orange pigment precipitate obtained was filtered and recrystallized by using methanol.

**Yield:** 58%; **M.p.** = 270 °C (decomposed).

**FT–IR (in cm<sup>-1</sup>):** 3297 (–OH stretch), 1608 (–C=N, imine), 1541 (–C=N, benzothiazole), 1489 (aromatic ring), 1264 (C–O stretch), 731 (–C–S stretch).

**<sup>1</sup>H NMR (in DMSO):** 6.84 (d, 1H, *J* = 1.8 Hz), 7.37 (m, 4H), 7.47 (t, 4H), 7.59 (m, 4H), 7.93 (d, 2H, *J* = 7.8 Hz), 8.21 (m, 4H), 8.20 (d, 1H, *J* = 8.12 Hz), 9.12 (d, 2H, *J* = 11.1 Hz), 9.12 (s, 2H), 16.0 (d, –OH, hydrogen bonding).

**Mass: m/z:** 682 (*M*–1).

**HRMS and <sup>13</sup>C NMR (in DMSO):** Due to poor solubility of compound in DMSO we could not record <sup>13</sup>C NMR. As well as HRMS.

#### **Elemental Analysis:**

**Calculated:** C, 73.88; H, 3.84; N, 8.21; S, 9.39.

**Found:** C, 73.87; H, 3.85; N, 8.18; S, 9.38.

#### 2.3.5. Synthesis of 1,1'-((1*E*,1'*E*)-(1,3-phenylenebis(azanylylidene))bis(methanylylidene))bis(3-(benzo[d]thiazol-2-yl)naphthalen-2-ol) **6d**

A mixture of 3-(1,3-benzothiazol-2-yl)-2-hydroxynaphthalene-1-carbaldehyde (1.00 g, 3.3 mmol) and 1,3-diaminobenzene (0.18 g, 1.7 mmol) in ethanol was refluxed for 4 h. On cooling, brown pigment precipitate obtained was filtered and recrystallized by using methanol.

**Yield:** 51%; **M.p.** >300 °C.

**FT–IR (in cm<sup>-1</sup>):** 3055 (–OH stretch), 1619 (–C=N, imine), 1585 (–C=N, benzothiazole), 1488 (Aromatic ring), 1283 (C–O stretch), 751 (–C–S stretch).

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