



# New heterocyclic green, blue and orange dyes from indazole: Synthesis, tautomerism, alkylation studies, spectroscopic characterization and DFT/TD-DFT calculations



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## ABSTRACT

Tautomerism and alkylation studies on the green intermediate 2-(5-hydroxyimino-1-methyl-4,5-dihydro-1*H*-4-indazolylidene)-2-phenylacetonitrile led to the synthesis of new heterocyclic green, blue and orange dyes in high yields. The structures of all newly synthesized compounds were confirmed by spectral and analytical data. The optical properties of the dyes were spectrally characterized by using a UV–vis spectrophotometer and results show that they exhibited interesting photophysical properties. Solvent effects on the absorption spectra of these dyes have been studied and the absorption band in polar solvents undergoes a red shift. Density functional theory calculations of the dyes were performed to provide the optimized geometries and relevant frontier orbitals. Calculated electronic absorption spectra were also obtained by time-dependent density functional theory method.

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## 1. Introduction

Donor–acceptor (D–A) heterocyclic dyes are among the most important conjugated organic materials, and have attracted much academic and technological research interest. In these compounds the electron-donating and electron-accepting groups are connected through a  $\pi$ -conjugated linker. Tuning different donor moiety or acceptor moiety in a D–A molecule would modify its physical and chemical properties. They have been evaluated and employed in the new areas of information-recording materials [1], information-display media [2], or optoelectronic devices [3]. These dyes can also be applied to organic photoconductors [4], solar-energy utilizations [5], sensitizers [6], biomedical probe [7], photo-catalysts [8], and so on. Furthermore, donor–acceptor heterocyclic dyes have been used extensively in the preparation of disperse dyes with outstanding dischargeability on cellulose acetate. These dyes are characterized also by having generally excellent brightness and high extinction coefficients. These new trends of dye chemistry have been recently developed and these classes of dyes are of significant importance in high-technology industries.

On the other hand, indazole scaffolds show interesting

biological properties, such as anti-depressant [9], anti-inflammatory [10], anti-tumor [11] and anti-HIV activities [12]. Recently indazole nucleus become of interest as a key moiety of dyes [13] and fluorescent compounds [14–17].

In continuation of our previous study on the synthesis of new green dyes from indazole [13], in current work, we have synthesized some new green, blue and orange dyes via alkylation and oxidation studies on the green intermediate 2-(5-hydroxyimino-1-methyl-4,5-dihydro-1*H*-4-indazolylidene)-2-phenylacetonitrile in high yields. In addition, tautomerism, optical properties and DFT calculations of the dyes have also been examined.

## 2. Experimental

### 2.1. Materials

Methanol, ethyl acetate (EtOAc), tetrahydrofuran (THF), acetonitrile, dichloromethane (DCM), *N,N*-dimethylformamide (DMF), methyl iodide, dimethyl sulfate (DMS), potassium *tert*-butoxide, *tert*-butanol and benzyl cyanide were purchased from Merck. Potassium hydroxide was purchased from Sigma–Aldrich. All solvents were dried according to standard procedures. Compounds **1** and **3** were synthesized as in literature [18,13].

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## 2.2. Equipment

Absorption spectra were recorded on a Varian Cary 50-bio UV–visible spectrophotometer. UV–vis scans were recorded from 200 to 800 nm. Melting points were measured on an Electrothermalttype-9100 melting-point apparatus. The IR (as KBr discs) spectra were obtained on a Tensor 27 spectrometer and only noteworthy absorptions are listed. The  $^{13}\text{C}$  NMR (100 MHz) and the  $^1\text{H}$  NMR (400 MHz) spectra were recorded on a Bruker Avance DRX-400 Fourier-transformer spectrometer in DMSO- $d_6$  and  $\text{CDCl}_3$ . Chemical shifts are reported in parts per million downfield from TMS as the internal standard; coupling constant  $J$  is given in hertz. The mass spectra were recorded on a Varian Mat, CH-7 at 70 eV. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. All measurements were carried out at room temperature.

## 2.3. Computational methods

DFT calculations have been performed with the Gaussian 98 software package [19] by using the B3LYP hybrid functional [20] and the 6-311++G (d,p) basis set. Firstly, geometry of the compounds **3**, **4** and **5** was fully optimized in the MeOH solution.

Here, one of self-consistent reaction field methods, the sophisticated Polarized Continuum Model (PCM) [21] has been used for investigation of the solvent effects. The PCM calculations have been performed in the MeOH solution and the zero-point corrections were considered to obtain energies. Based on the optimized geometries and using time-dependent density functional theory (TD-DFT) [22–24] methods, the electronic spectra of the compounds **3**, **4** and **5** were predicted.

## 2.4. Synthesis of 2-(1-methyl-5-nitroso-1H-indazol-4-yl)-2-phenylacetoneitrile (4)

Compound **3** (5.0 g, 18 mmol) was heated 4 h under reflux in EtOAc or other solvents such as  $\text{CHCl}_3$ , MeCN and MeOH (80 mL). Also, dye **3** converts to **4** under the influence of visible light after 2 days in above mentioned solvents at rt. Furthermore, the process can catalyze in acidic media (pH 2–6,  $\text{H}_2\text{O}$ –MeOH, 95:5) and takes place in less than 4 h.

After concentration the blue solution at reduced pressure, the precipitate was collected by filtration, washed with water and then air dried to give dark blue powder **4**. More purification was achieved by recrystallization from acetone.

Yield (90%), mp 135–137 °C;  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  4.21 (s, 3H, N– $\text{CH}_3$ ), 6.54 (s, 1H, benzylic CH), 7.24–7.30 (m, 3H, Ar H), 7.33–7.37 (m, 2H, Ar H), 7.48 (d,  $J = 9.5$  Hz, 1H, Ar H), 8.53 (d,  $J = 9.5$  Hz, 1H, Ar H), 8.65 (s, 1H, Ar H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  35.6, 36.7, 107.3, 112.3, 125.8, 127.9, 131.0, 133.2, 133.8, 134.6, 143.5, 149.4, 151.0, 167.2; IR (KBr): 2340  $\text{cm}^{-1}$  (CN), 1535  $\text{cm}^{-1}$  (N=O). MS ( $m/z$ ) 276 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}$  (276.3): C, 69.55; H, 4.38; N, 20.28. Found: C, 69.27; H, 4.36; N, 20.07.

## 2.5. Synthesis of 2-(1-methyl-5-nitro-1H-indazol-4-yl)-2-phenylacetoneitrile (5)

To a stirred solution of dye **4** (2.76 g, 10 mmol) in MeOH (10.0 mL) were added 30%  $\text{H}_2\text{O}_2$  (5.5 mL, 21 mmol) at 60 °C. After the 4 h, the orange solution was diluted with  $\text{H}_2\text{O}$  (50 mL), chilled and filtered, and then the solid was washed with  $\text{H}_2\text{O}$  and air dried to give crude **5**. Dye **5** was recrystallized from MeOH. Yield (85%), mp 156–159 °C;  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  4.23 (s, 3H, N– $\text{CH}_3$ ), 6.61 (s, 1H, benzylic CH), 7.26–7.34 (m, 3H, Ar H), 7.37–7.40 (m, 2H, Ar H), 7.43 (d,  $J = 9.5$  Hz, 1H, Ar H), 8.61 (s, 1H, Ar H), 8.69 (d,  $J = 9.5$  Hz, 1H,

Ar H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  37.1, 39.6, 105.6, 110.1, 125.7, 125.9, 131.6, 133.5, 133.9, 134.2, 142.4, 149.4, 151.3, 167.6; IR (KBr): 2345  $\text{cm}^{-1}$  (CN), 1335, 1545  $\text{cm}^{-1}$  ( $\text{NO}_2$ ). MS ( $m/z$ ) 292 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2$  (292.3): C, 69.75; H, 4.14; N, 19.17. Found: C, 69.52; H, 4.11; N, 18.95.

## 2.6. Synthesis of 5-(methoxyimino)-1-methyl-1H-indazol-4(5H)-ylidene)-2-phenylacetoneitrile (6)

To a green solution of dye **3** (1.4 g, 5 mmol) in acetonitrile (50 mL), dimethyl sulfate (DMS) (0.9 g, 7 mmol) and  $\text{K}_2\text{CO}_3$  (5.5 g, 40 mmol) were added. The mixture was stirred for 12 h at rt and then poured into water. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  50 mL). The extract was dried ( $\text{MgSO}_4$ ), treated with charcoal and evaporated to give crude **6**. More purification was achieved by recrystallization from MeOH– $\text{H}_2\text{O}$  (1:1).

Yield (75%), mp 125–127 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.21 (s, 3H, N– $\text{CH}_3$ ), 4.31 (s, 3H, O– $\text{CH}_3$ ), 7.33–7.37 (m, 2H, Ar H), 7.48 (d,  $J = 9.5$  Hz, 1H, Ar H), 7.55 (d,  $J = 9.5$  Hz, 1H, Ar H), 7.59–7.61 (m, 2H, Ar H), 7.79 (t,  $J = 8.0$  Hz, 1H, Ar H), 8.21 (s, 1H, Ar H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  36.3, 65.7, 108.8, 114.2, 121.6, 122.6, 125.0, 128.1, 129.7, 130.8, 131.2, 135.4, 145.2, 153.5, 162.0; IR (KBr): 2220  $\text{cm}^{-1}$  (CN). MS ( $m/z$ ) 290 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}$  (290.3): C, 70.33; H, 4.86; N, 19.30. Found: C, 70.19; H, 4.83; N, 19.11.

## 2.7. Synthesis of 2-(1-methyl-5-nitroso-1H-indazol-4-yl)-2-phenylpropanenitrile (7)

Methyl iodide (1.4 g, 10 mmol) and potassium *tert*-butoxide (1.12 g, 10 mmol) were added to a solution of compound **4** (2.76 g, 10 mmol) in *tert*-butanol (50 mL). After the mixture was stirred for 4 h at rt, it poured into water. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  40 mL). The extract was dried ( $\text{MgSO}_4$ ), treated with charcoal and evaporated to give crude **7**. More purification was performed by recrystallization from *n*-hexane–EtOAc (1:1).

Yield (60%), mp 131–134 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.15 (s, 3H,  $\text{CH}_3$ ), 4.23 (s, 3H, N– $\text{CH}_3$ ), 7.21–7.27 (m, 3H, Ar H), 7.34–7.38 (m, 2H, Ar H), 7.51 (d,  $J = 9.5$  Hz, 1H, Ar H), 8.49 (d,  $J = 9.5$  Hz, 1H, Ar H), 8.62 (s, 1H, Ar H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  30.4, 35.5, 44.2, 107.9, 111.6, 126.5, 128.3, 131.3, 133.4, 133.9, 134.6, 143.2, 149.7, 151.2, 167.8; IR (KBr): 2345  $\text{cm}^{-1}$  (CN), 1545  $\text{cm}^{-1}$  (N=O). MS ( $m/z$ ) 290 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}$  (290.3): C, 70.33; H, 4.86; N, 19.30. Found: C, 70.17; H, 4.82; N, 19.19.

## 3. Results and discussion

### 3.1. Synthesis and structure of the new dyes 4–7

As depicted in Scheme 1, 1-methyl-5-nitro-1H-indazole (**1**) was prepared by reaction of 5-nitro-1H-indazole with methyl iodide in DMF and KOH using literature method [18]. The reaction of 1-methyl-5-nitro-1H-indazole with benzyl cyanide (**2**) led to the formation of key intermediate 2-(5-hydroxyimino-1-methyl-4,5-dihydro-1H-4-indazolylidene)-2-phenylacetoneitriles (**3**) via the nucleophilic substitution of hydrogen [25–27] in basic methanol solution in excellent yield (Scheme 1). The structure of dye **3** has been established by DFT calculations previously [13].

When compound **3** was heated under reflux in EtOAc or other solvents such as  $\text{CHCl}_3$  and MeCN, new blue dye **4** was obtained in excellent yield (Scheme 2).

The structure of the new synthesized compound **4** was deduced from their spectral and microanalytical data. For example, the IR spectrum of **4** showed a stretching vibration band at 1535  $\text{cm}^{-1}$  indicating for N=O group. The  $^1\text{H}$  NMR spectrum of **4** showed three distinguished singlet signals at  $\delta$  4.21, 6.54 and 8.65 ppm for

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