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Synthesis, DFT calculations and cyclic voltammetry analysis of new heterocyclic green dyes: 2-(5-Hydroxyimino-1-alkyl-4,5-dihydro-1*H*-4-indazolyliden)-2-arylacetonitriles

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New derivatives of 2-(5-hydroxyimino-1-alkyl-4,5-dihydro-1*H*-4-indazolyliden)-2-arylacetonitriles were synthesized by the reaction of 1-alkyl-5-nitro-1*H*-indazole with different arylacetonitriles *via* nucleophilic substitution of hydrogen. The structures of all newly synthesized compounds were confirmed by IR, ^{1}H NMR, ^{13}C NMR and Mass spectral data. The compounds were deep green in color and their color intensity indicates intramolecular charge transfer (ICT) states from the donor site (OH group) to the acceptor moiety (CN group). The absorption spectra of these dyes are similar to each other and the values of extinction coefficient for them are too large. Solvent effects on absorption spectra of these dyes have been studied and the absorption band in protic solvents undergoes a bathochromic shift. Density function theory (DFT) calculations of one structure by using the B3LYP hybrid functional and the 6-311 + G (d,p) basis set to provide the relevant frontier orbitals and cyclic voltammetry analysis were also performed.

1. Introduction

Various numbers of chromophores have been investigated to achieve satisfactory characteristics in terms of functional applications and specialized uses. Organic colorants 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. These new trends of dye chemistry have been recently developed and these classes of dyes are of significant importance in high-technology industries. There is a myriad of examples of synthetic colors, products of the chemical manufacturing industry, which commonly serve a purely decorative or aesthetic purpose, but in some cases specific colors may be used to convey vital information, for example in traffic lights and color coded electrical cables.

The most important green organic dyes are Malachite Green, Methyl Green, SYBR Green II [9,10], Pico Green, SYTOX Green cyanine dye [11] and SYBR Green I (SG) which is probably the most widely used dye in real-time polymerase chain reaction (PCR) [12] for clinical analysis and melting-curve analysis [13].

In continuation of our previous studies on the synthesis of new dyes [14–19], here, the synthesis of new donor–acceptor green dyes by the reaction of 1-alkyl-5-nitro-1*H*-indazole with arylacetonitriles *via* nucleophilic substitution of hydrogen [20–23], evaluation of their spectroscopic properties, DFT calculations and cyclic voltammetry analysis are reported. Donor–acceptor (D–A) organic molecules are among the most important conjugated organic materials, and have attracted much academic and technological research interest [24]. In these compounds the electron-donating and electron-accepting groups are connected through a π-conjugated linker. Tuning different donor moiety or acceptor moiety in a D–A molecule would modify its physical and chemical properties.

2. Experimental

2.1. Materials

Methanol, ethanol, ethyl acetate, 1,4-dioxane, acetone, acetonitrile, dichloromethane (DCM), N,N-Dimethyl formamide (DMF), methyl iodide, ethyl bromide, n-propyl bromide, n-butyl bromide, phenylacetonitrile and 2-(4-methylphenyl)acetonitrile were purchased from

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Merck. 2-(4-Chlorophenyl)acetonitrile, tetrabutylammonium perchlorate (TBAP) and potassium hydroxide were purchased from Sigma–Aldrich. All solvents were dried according to standard procedures. Compounds **1a-d** were synthesized as in literature [25].

2.2. Equipment

Absorption spectra were recorded on a Varian Cary 50-bio UV–visible spectrophotometer. UV–*vis* scans were recorded from 200 to 1000 nm. Melting points were measured on an Electrothermaltype-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}C NMR (100 MHz) and the ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance DRX-400 Fouriertransformer spectrometer in DMSO. 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. Cyclic voltammograms were recorded on a 797 VA Computrace Metrohm. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte and a platinum wire served as a counter electrode and a silver wire contained in a glass tube was utilized as a reference electrode. The concentrations used to obtain each voltammogram are given in the corresponding figure caption.

2.3. Computational methods

DFT calculations have been performed with the Gaussian 98 software package [26] by using the B3LYP hybrid functional [27] and the 6-311 + G (d,p) basis set. Firstly, geometry of the compound **3c** was fully optimized in the DMSO solution. The optimized geometry was confirmed to have no imaginary frequency of the Hessian. Then, its optimized geometry was used for frequency, NMR and NBO calculations.

Here, one of self-consistent reaction field methods, the sophisticated Polarized Continuum Model (PCM) [28] has been used for investigation of the solvent effects. The PCM calculations have been performed in the DMSO solution and the zero-point corrections were considered to obtain energies.

The ^{1}H NMR chemical shifts of the **3c** were predicted with respect to tetramethylsilane (TMS). Here, the GIAO method was used for prediction of DFT nuclear shielding [29].

2.4. General procedure for the synthesis of *3a-f* from *1a-d* and *2a-c*

To a solution of KOH (20 g, 357 mmol) in methanol (80 mL) compounds **1a-d** (10 mmol) and **2a-c** (12 mmol) were added with stirring. The mixture was refluxed with stirring for 2 h, and then poured into water and then it was neutralized with dilute HCl solution. The precipitate was collected by filtration, washed with water, following with n-hexane-dichloromethane (50:50), and then air dried to give practically pure **3a-f**. More purification was achieved by crystallization from suitable solvent such as n-hexane-ethyl acetate or acetone.

2.4.1. 2-(5-Hydroxyimino-1-methyl-4,5-dihydro-1H-4 indazolyliden)-2-phenylacetonitrile (*3a*)

Compound **3a** was obtained as dark green powder (n-hexane-ethyl acetate), yield (65%), mp 140–142 °C; ^{1}H NMR (DMSO-d_6) δ 4.15 (s, 3H), 7.31–7.35 (m, 2H), 7.51 (d, $J = 9.5$ Hz, 1H), 7.58 (d, $J = 9.5$ Hz, 1H), 7.69–7.73 (m, 2H), 7.85 (tt, $J_1 = 8.0$ Hz, $J_2 = 2.1$ Hz, 1H), 8.18 (s, 1H), 13.41 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 36.69, 108.41, 115.12, 121.89, 122.98, 125.04, 128.69,129.23, 130.11, 130.82, 135.44, 145.82, 153.87, 162.07; IR (KBr): 3450 cm^{-1} (OH), 2210 cm^{-1} (CN). MS (m/z) 276 (M^{+}). Anal. Calcd for $C_{16}H_{12}N_4O$ (276.3): C, 69.55; H, 4.38; N, 20.28. Found: C, 69.12; H, 4.34; N, 19.93.

2.4.2. 2-(5-Hydroxyimino-1-methyl-4,5-dihydro-1H-4 indazolyliden)-2-(4 methylphenyl)acetonitrile (*3b*)

Compound **3b** was obtained as green powder (n-hexane-ethyl acetate), yield (71%), mp 137–139 °C; ^{1}H NMR (DMSO-d_6) δ 2.35 (s, 3H), 4.18 (s, 3H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 9.5$ Hz, 1H), 7.53 (d, $J = 9.5$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 2H), 8.14 (s, 1H), 13.27 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 22.07, 36.41, 108.21, 116.65, 121.23, 121.95, 125.90, 129.54, 129.87, 130.89, 133.95, 140.44, 145.90, 154.12, 161.23; IR (KBr): 3455 cm^{-1} (OH), 2202 cm^{-1} (CN). MS (m/z) 290 (M^{+}). Anal. Calcd for $C_{17}H_{14}N_4O$ (290.3): C, 70.33; H, 4.86; N, 19.30. Found: C, 70.67; H, 4.90; N, 18.98.

2.4.3. 2-(4-Chlorophenyl)-2-(5-hydroxyimino-1-methyl-4,5-dihydro-1H-4 indazolyliden)acetonitrile (*3c*)

Compound **3c** was obtained as dark green powder (acetone), yield (80%), mp 150–152 °C; ^{1}H NMR (DMSO-d_6) δ 4.17 (s, 3H), 7.48 (d, $J = 9.6$ Hz, 1H), 7.55 (d, $J = 9.6$ Hz, 1H), 7.61 (d, $J = 8.3$ Hz, 2H), 7.98 (d, $J = 8.3$ Hz, 2H), 8.16 (s, 1H), 13.35 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 36.50, 108.53, 115.76, 121.50, 122.43, 125.91, 129.12, 129.92, 130.23, 130.62, 135.45, 145.87, 154.03, 161.59; IR (KBr): 3450 cm^{-1} (OH), 2196 cm^{-1} (CN). MS (m/z) 312 (M^{+} + 2). Anal. Calcd for $C_{16}H_{11}ClN4O$ (310.7): C, 61.84; H, 3.57; N, 18.03. Found: C, 61.61; H, 3.43; N, 18.41.

2.4.4. 2-(4-Chlorophenyl)-2-(1-ethyl-5-hydroxyimino-4,5-dihydro-1H-4-indazolyliden)acetonitrile (*3d*)

Compound **3d** was obtained as dark green powder (n-hexane-ethyl-acetate), yield (82%), mp 145–147 °C; ^{1}H NMR (DMSO-d_6) δ 1.69 (t, $J = 7.2$ Hz, 3H), 4.65 (q, $J = 7.2$ Hz, 2H), 7.50 (d, $J = 9.6$ Hz, 1H), 7.56 (d, $J = 9.6$ Hz, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 8.15 (s, 1H), 13.55 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 14.07, 45.55, 108.51, 115.78, 121.51, 122.43, 125.90, 129.09, 129.89, 130.25, 130.64, 135.45, 145.87, 154.07, 161.58; IR (KBr): 3455 cm^{-1} (OH), 2195 cm^{-1} (CN). MS (m/z) 326 (M^{+} + 2). Anal. Calcd for $C_{17}H_{13}ClN_4O$ (324.8): C, 62.87; H, 4.03; N, 17.25. Found: C, 62.55; H, 3.93; N, 16.92.

2.4.5. 2-(4-Chlorophenyl)-2-(5-hydroxyimino-1-propyl-4,5-dihydro-1H-4 indazolyliden)acetonitrile (*3e*)

Compound **3e** was obtained as dark green powder (n-hexane-ethyl-acetate), yield (75%), mp 134–137 °C; ^{1}H NMR (DMSO-d_6) δ 0.87 (t, $J = 7.2$ Hz, 3H), 1.85–1.93 (m, 2H), 4.35 (t, $J = 7.2$ Hz, 2H), 7.50 (d, $J = 9.6$ Hz, 1H), 7.56 (d, $J = 9.6$ Hz, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 8.16 (s, 1H), 13.51 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 13.14, 23.05, 52.93, 108.52, 115.79, 121.52, 122.43, 125.90, 129.08, 129.89, 130.26, 130.65, 135.45, 145.87, 154.09, 161.56; IR (KBr): 3455 cm^{-1} (OH), 2195 cm^{-1} (CN). MS (m/z) 340 (M^{+} + 2). Anal. Calcd for $C_{18}H_{15}ClN_4O$ (338.8): C, 63.81; H, 4.46; N, 16.54. Found: C, 63.50; H, 4.39; N, 16.38.

2.4.6. 2-(1-Butyl-5-hydroxyimino-4,5-dihydro-1H-4-indazolyliden)-2-(4-chlorophenyl)acetonitrile (*3f*)

Compound **3f** was obtained as dark green powder (n-hexane-ethyl-acetate), yield (70%), mp 125–127 °C; ^{1}H NMR (DMSO-d_6) δ 0.91 (t, $J = 7.1$ Hz, 3H), 1.31–1.41 (m, 2H), 1.92–2.02 (m, 2H), 4.35 (t, $J = 7.1$ Hz, 2H), 7.50 (d, $J = 9.6$ Hz, 1H), 7.57 (d, $J = 9.6$ Hz, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.96 (d, $J = 8.3$ Hz, 2H), 8.16 (s, 1H), 13.27 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 14.92, 20.61, 33.50, 48.01, 108.52, 115.79, 121.53, 122.43, 125.89, 129.06, 129.89, 130.28, 130.65, 135.45,