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Phenylazoindole dyes 3: Determination of azo-hydrazone tautomers of new phenylazoindole dyes in solution and solid state



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HIGHLIGHTS

- Two series of new phenylazo indole dyes were efficiently synthesized and characterized.
- The most stable tautomeric form of the dyes was determined as experimental and theoretical in solution, gas phase and solid state.
- The experimental results are compatible with the theoretical results.

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Introduction

Azo colorants are the most widely used class of dyes because of their synthetic facilities, good stabilities/fastnesses and large color ranges [1-3]. They have been used as dyes owing to their versatilities in various fields and high technologies which include textile fibers, chemosensors, coloring different materials, biological-

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ABSTRACT

A new two series of phenylazo indole dyes was synthesized and the structures of the dyes were confirmed by UV-vis, FT-IR, HRMS and ${}^{1}H/{}^{13}C$ NMR spectroscopic techniques. Five of these dyes (I, I', II', III and III') were also characterized in solid state by using single crystal X-ray diffraction studies besides other spectroscopic techniques. The geometries of the azo and hydrazone tautomeric forms of the dyes were optimized by using Density Functional Theory (DFT). In addition, the effects of the donor and acceptor groups on the azo and hydrazone forms of the dyes were evaluated experimentally and theoretically. The results indicate that the phenylazoindole dyes derived from 2-phenyl indole as coupling component exist as azo form in solution, gas phase and solid state.

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medicinal studies, non-linear optics (NLO) and optical data storage [1,4–7]. However, the some of dyes include azo chromophoric system release of carcinogenic amines after reductive cleavage to environment [8]. Their optical, technical, environmental and application performances of azo dyes are strongly related to their tautomeric equilibriums, molecular structures and spectroscopic properties in solution and solid state [9–12]. Hence, the study of azo-hydrazone tautomerism is one of the most interesting research field in dye chemistry [13–15].

In our earlier studies, we have synthesized and determined the tautomeric behaviors of a number of aryl/heteroarylazo indole dyes in solution and solid state [16–22] Fig. 1.

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Fig. 1. Tautomeric forms of previous synthesized hetarylazoindole dye [22].



Scheme 1. The synthetic pathway of the dyes (I-VI and I'-VI').

In the current communication, we synthesized two series of phenylazoindole dyes by using traditional azo coupling between 2- or 1,2-disubstituted indoles and diazonium salts of para substituted aniline derivatives. The first series of compounds include 2-phenyl indole (I-VI) as coupling component can exist in two possible tautomeric forms namely azo and hydrazone forms. The second series include 1-methyl-2-phenyl indole (I-VI) as coupling component dyes (I'-VI') exist only in azo form (Scheme 1). Thus, the dyes derived from 1-methyl-2-phenyl indole will be used as model compound for the first series of compounds to determine their tautomeric behaviors in solution and solid state. This manuscript mainly includes the exploration of the azo-hydrazone tautomerism of the dyes experimentally and theoretically in solution and solid state. The UV-vis absorption spectra of these dyes in different solvents were studied and the effects of the solvents and the substituents on the azo/hydrazone tautomeric equilibrium were also evaluated.

Experimental section

Materials and instrumentation

The chemical used in the syntheses of all dyes were obtained from Aldrich Chemical Company (USA) and were used without further purification. FT-IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer (Gazi University Department of Chemistry, Turkey) in KBr (v, in cm⁻¹). ¹H NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 400 MHz Ultra-Shield (Hacettepe University, Department of Chemistry, Turkey) in DMSO-d₆ with TMS as the internal reference. Chemical shifts were expressed in δ units (ppm). Ultraviolet-visible (UV-vis) absorption spectra were recorded on an Analytikjena Specord 200 Spectrophotometer (Gazi University, Department of Chemistry, Turkey) at the wavelength of maximum absorption (λ_{max} , in nm) in range of solvents, i.e. dimethylsulfoxide (DMSO, ε , 46.45), methanol (ε , 32.66), acetic acid (ε , 6.17) and chloroform (ε , 4.81). All melting points were uncorrected and in °C (Electrothermal 9200 melting point apparatus). Mass analyses were done on a Waters LCT Premier XE (TOF MS) (Gazi University Laboratories, Department of Pharmacological Sciences).

Computational study

All quantum chemical calculations were performed using the GAUSSIAN 09 software [23]. The ground state geometries of azohydrazone tautomers of the dyes **I–IV** and their related model compounds **I'–IV**['] were optimized using the Density Functional Theory (DFT) with the B3LYP/6311+g(d,p) [24]. The frequency analyses indicate that the optimized geometries were in a minimum of the potential surface with no imaginary frequencies. Time Dependent Density Functional Theory (TD-DFT) computations [25] were used to obtain the vertical excitation energies and oscillator strengths at the optimized ground state equilibrium geometries and at the same hybrid functional and basis sets. All the computations in solvents of different polarities were carried out using the Self-Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM) [26].

Crystallography analyses

For the crystal structure determinations, the single-crystals of the compounds **I**, **I'**, **II'**, **III** and **III'** were used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and oscillation scans technique with $\Delta w = 5^{\circ}$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, corrections for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc., 2005) software [27]. The structures were solved by direct methods using SHELXS-97 [27] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [28]. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance.

Synthesis of the dyes

Diazotization of various aniline derivatives was affected with HCl and NaNO₂. A typical procedure is that which is described in below; all compounds (I-IV and I'-IV') were prepared in a similar



Scheme 2. Possible tautomeric forms of the phenylazo indole dyes in different solvents and pH.

manner (Scheme 2). The compounds were purified by recrystallization from ethanol. Characterization data, melting points and yields of the dyes are given in below.

General synthetic procedure

The proper aniline or derivative (2.0 mmol) was dissolved in hydrochloric acid (1.5 mL conc. HCl in 4 mL water). The solution was then cooled to $0-5 \,^{\circ}$ C with stirring. Sodium nitrite (0.15 g, 2.0 mmol) in water (3 mL) was gradually added to this solution over 15 min period at $0-5 \,^{\circ}$ C with stirring. The mixture was stirred for an additional 1 h at $0-5 \,^{\circ}$ C. Excess nitrous acid was destroyed by addition of urea. Indole derivatives which is used as coupling component (2.0 mmol) was dissolved in acetic acid/propionic acid (7 mL, ratio 5:2) and cooled to $0-5 \,^{\circ}$ C in a salt/ice bath. The cold diazonium salt solution was added to this cooled solution over 15 min with vigorous stirring in a dropwise manner, while maintaining the pH at 4-6 by addition of diluted NaOH solution. The mixture was further stirred for 1 h at $0-5 \,^{\circ}$ C and resulting solid was filtered, washed with cold water, dried, and recrystallized from ethanol.

3-(Phenyldiazenyl)-2-phenyl-1H-indole (I)

This dye was obtained from aniline and 2-phenyl-1H-indole. Yield: 78%, m.p.: 159–160, FT-IR (KBr) v_{max} (cm⁻¹): 3406 (N–H), 3055 (aromatic C–H), 2925 (aliphatic C–H), 1490 (C=C), 1389 (N=N); ¹H NMR (DMSO-*d*₆): δ 12.40 (brs, N–H), 8.51 (d, 1H, *J* = 7.79 Hz), 8.17 (d, 2H, *J* = 7.91 Hz), 7.82 (d, 2H, *J* = 8.08 Hz), 7.62 (m, 2H), 7.55 (m, 4H), 7.43–7.25 (m, 3H); ¹³C NMR (DMSO-*d*₆): 154.23, 142.91, 136.11, 132.11, 131.10, 129.97, 129.72, 129.59, 129.22, 129.16, 124.74, 123.42, 123.28, 121.25, 119.45, 112.44; HRMS (m/z): found 298.1333 (calculated: 298.1344) for $C_{20}H_{16}N_3^+$, $[M-H]^+$.

3-(4-Methoxyphenyldiazenyl)-2-phenyl-1H-indole (II)

This dye was obtained from 4-methoxyaniline and 2-phenyl-1H-indole. Yield: 81%, m.p.: 180–182, FT-IR (KBr) v_{max} (cm⁻¹): 3406 (N—H), 3191 (aromatic C—H), 2920 (aliphatic C—H), 1599 (C=C), 1370 (N=N), 1232 (C=O); ¹H NMR (DMSO-*d*₆): δ 12.40 (brs, N—H), 8.49 (d, 1H, *J* = 7.79 Hz), 8.17 (d, 2H, *J* = 8.41 Hz), 7.80 (d, 2H, *J* = 8.94 Hz), 7.60 (m, 2H), 7.51 (m, 2H), 7.30–7.20 (m, 2H), 7.11 (d, 2H); ¹³C NMR (DMSO-*d*₆): 160.28, 148.49, 131.89, 129.81, 129.34, 129.18, 129.04, 125.45, 124.30, 123.35, 123.20, 122.88, 119.69, 114.92, 112.66, 55.91; HRMS (*m*/*z*): found 328.1450 (calculated: 328.1450) for C₂₁H₁₈N₃O⁺, [M–H]⁺.

3-(4-Methylphenyldiazenyl)-2-phenyl-1H-indole (III)

This dye was obtained from 4-methylaniline and 2-phenyl-1Hindole. Yield: 74%, m.p.: 152–153, FT-IR (KBr) v_{max} (cm⁻¹): 3395 (N—H), 3069 (aromatic C—H), 2971–2925 (aliphatic C—H), 1598 (C=C), 1385 (N=N); ¹H NMR (DMSO-*d*₆): δ 12.33 (brs, N—H), 8.49 (d, 1H, *J* = 7.79 Hz), 8.16 (d, 2H, *J* = 7.23 Hz), 7.73 (d, 2H, *J* = 7.03 Hz), 7.62 (t, 2H, *J* = 7.43 Hz), 7.54–7.50 (m, 2H), 7.38 (d, 2H, *J* = 7.36 Hz), 7.34–7.23 (m, 2H); ¹³C NMR (DMSO-*d*₆): 152.25, 142.25, 139.03, 136.44, 131.94, 131.16, 130.25, 129.87, 129.49, 129.34, 129.14, 125.44, 124.65, 123.27, 121.90, 119.48, 112.35; HRMS (*m*/*z*): found 312.1502 (calculated: 312.1501) for C₂₁H₁₈N⁺₃, [M–H]⁺.

3-(4-Chlorophenyldiazenyl)-2-phenyl-1H-indole (IV)

This dye was obtained from 4-chloroaniline and 2-phenyl-1Hindole. Yield: 73%, m.p.: 153–155, IR (KBr) v_{max} (cm⁻¹): 3413 (N—H), 3061 (aromatic C—H), 1476 (C=C), 1372 (N=N); ¹H NMR (DMSO-*d*₆): δ 11.65 (brs, N—H), 8.37 (d, 1H, *J* = 7.54 Hz), 7.94 (d, 2H, *J* = 7.39 Hz), 7.60 (d, 2H, *J* = 8.47 Hz), 7.38–7.20 (m, 6H), 7.12– 7.04 (m, 2H); ¹³C NMR (DMSO-*d*₆): 152.84, 143.47, 136.45, 133.37, 132.14, 130.85, 130.02, 129.79, 129.21, 124.94, 123.62, 123.51, 123.29, 119.33, 112.45; HRMS (*m/z*): found 332.0949 (calculated: 332.0955) for C₂₀H₁₅ClN⁺₃, [M–H]⁺.

3-(4-Cyanophenyldiazenyl)-2-phenyl-1H-indole (**V**)

This dye was obtained from 4-cyanoaniline and 2-phenyl-1H-indole. Yield: 71%, m.p.: 293–294, FT-IR (KBr) v_{max} (cm⁻¹): 3293 (N—H), 3052 (aromatic C—H), 2227 (C=N), 1595 (C=C), 1364 (N=N); ¹H NMR (DMSO- d_6): δ 12.60 (brs, N—H), 8.50 (d, 1H, J = 7.03 Hz), 8.16 (d, 2H, J = 7.44 Hz), 7.98 (d, 2H, J = 8.46 Hz), 7.92 (d, 2H, J = 8.56 Hz), 7.63 (t, 2H, J = 7.30 Hz), 7.56 (t, 2H, J = 7.97 Hz), 7.33 (m, 2H); ¹³C NMR (DMSO- d_6): 156.65, 145.26, 136.62, 134.09, 132.96, 130.52, 130.24, 130.15, 129.27, 125.33, 124.12, 123.42, 122.56, 119.46, 119.17, 112.64, 110.58; HRMS (m/z): found 323.1294 (calculated: 323.1297) for C₂₁H₁₅N⁺, [M–H]⁺.

3-(4-Nitrophenyldiazenyl)-2-phenyl-1H-indole (VI)

This dye was obtained from 4-nitroaniline and 2-phenyl-1Hindole. Yield: 70%, m.p.: 290–291, IR (KBr) v_{max} (cm⁻¹): 3415 (N—H), 3039 (aromatic C—H), 1600–1530 (C=C), 1376 (N=N); ¹H NMR (DMSO-*d*₆): δ 12.70 (brs, N—H), 8.53 (d, 1H, *J* = 7.64 Hz), 8.37 (d, 2H, *J* = 8.91 Hz), 8.17 (d, 2H, *J* = 7.47 Hz), 7.97 (d, 2H, *J* = 8.91 Hz), 7.67–7.52 (m, 4H), 7.38 (t, 1H, *J* = 6.96 Hz), 7.33 (t, 1H, *J* = 7.17 Hz); ¹³C NMR (DMSO-*d*₆): 158.16, 146.67, 145.99, 136.84, 130.48, 130.31, 130.25, 129.28, 125.51, 125.46, 124.28, 123.48, 122.51, 119.17, 112.77; HRMS (*m*/*z*): found 343.1198 (calculated: 343.1195) for C₂₀H₁₅N₄O⁺, [M–H]⁺.

3-(Phenyldiazenyl)-1-methyl-2-phenyl-1H-indole (I')

This dye was obtained from aniline and 1-methyl-2-phenyl-1H-indole. Yield: 81%, m.p.: 136–137, FT-IR (KBr) v_{max} (cm⁻¹): 3052 (aromatic C—H), 2928 (aliphatic C—H), 1472 (C=C), 1383 (N=N); ¹H NMR (DMSO-*d*₆): δ 8.53 (d, 1H, *J* = 7.43 Hz), 7.76 (d, 2H, *J* = 6.69 Hz), 7.55–7.68 (m, 6H), 7.30–7.50 (m, 5H), 3.85 (s, 3H, —N—CH₃); ¹³C NMR (DMSO-*d*₆): 154.04, 146.94, 137.59, 132.17, 132.01, 129.67, 129.58, 129.51, 129.13, 128.61, 124.65, 123.81, 122.89, 121.78, 118.33, 111.22, 32.05; HRMS (*m/z*): found 312.1490 (calculated: 312.1501) for C₂₁H₁₈N⁺₃, [M–H]⁺.

3-(4-Methoxyphenyldiazenyl)-1-methyl-2-phenyl-1H-indole (II')

This dye was obtained from 4-methoxyaniline and 1-methyl-2-phenyl-1H-indole. Yield: 84%, m.p.: 165–167, FT-IR (KBr) v_{max} (cm⁻¹): 3063 (aromatic C—H), 2975 (aliphatic C—H), 1478 (C=C), 1378 (N=N), 1252 (C—O); ¹H NMR (DMSO-*d*₆): δ 8.52 (d, 1H, *J* = 7.88 Hz), 7.75 (dd, 2H, *J*₁ = 8.19 Hz, *J*₂ = 1.20 Hz), 7.68–7.58 (m, 6H), 7.40 (td, 1H *J*₁ = 6.96 Hz, *J*₂ = 1.25 Hz), 7.32 (t, 1H, *J* = 8.32 Hz), 7.05 (d, 2H, *J* = 7.08 Hz), 3.84 (s, 3H, —OCH₃), 3.83 (s, 3H, —N—CH₃); ¹³C NMR (DMSO-*d*₆): 160.36, 148.24, 145.71, 137.51, 131.98, 129.74, 129.48, 128.58, 124.43, 123.44, 123.29, 122.91, 118.47, 114.80, 111.09, 55.88, 31.98; HRMS (*m*/*z*): found 342.1595 (calculated: 342.1606) for C₂₂H₂₀N₃O⁺, [M–H]⁺.

3-(4-Methylphenyldiazenyl)-1-methyl-2-phenyl-1H-indole (III')

This dye was obtained from 4-methylaniline and 1-methyl-2phenyl-1H-indole. Yield: 82%, m.p.: 122–124, FT-IR (KBr) v_{max} (cm⁻¹): 3040 (aromatic C–H), 2920 (aliphatic C–H), 1467 (C=C), 1382 (N=N); ¹H NMR (DMSO-*d*₆): δ 8.52 (d, 1H, *J* = 7.76 Hz), 7.75 (d, 2H, *J* = 7.52 Hz), 7.69–7.57 (m, 6H), 7.40 (t, 1H, *J* = 7.17 Hz) 7.35–7.27 (m, 3H), 3.81 (s, 3H, $-N-CH_3$), 2.32 (s, 3H, $-CH_3$); ¹³C NMR (DMSO-*d*₆): 152.08, 146.39, 138.88, 137.55, 132.00, 130.10, 129.61, 128.60, 124.55, 123.65, 122.90, 121.74, 118.39, 111.18, 95.69, 32.04, 21.34; HRMS (*m*/*z*): found 326.1652 (calculated: 326.1657) for C₂₂H₂₀N⁺₃, [M–H]⁺.

3-(4-Chlorophenyldiazenyl)-1-methyl-2-phenyl-1H-indole (**IV**)

This dye was obtained from 4-chloroaniline and 1-methyl-2-phenyl-1H-indole. Yield: 72%, m.p.: 169–170, FT-IR (KBr) v_{max} (cm⁻¹): 3012 (aromatic C—H), 2987 (aliphatic C—H), 1466 (C=C), 1375 (N=N); ¹H NMR (DMSO-*d*₆): δ 8.52 (d, 1H, *J* = 7.65 Hz), 7.63 (m, 5H), 7.52 (m, 2H), 7.43 (d, 1H, *J* = 7.90 Hz), 7.35–7.24 (m, 4H), 3.80 (s, 3H, $-N-CH_3$); ¹³C NMR (DMSO-*d*₆): 152.21, 146.97, 137.16, 132.72, 131.80, 131.50, 129.28, 129.16, 128.87, 128.15, 124.30, 123.50, 122.81, 122.42, 117.78, 110.82, 31.62; HRMS (*m*/*z*): found 346.1111 (calculated: 346.1111) for C₂₁H₁₇ClN³₃, [M–H]⁺.

3-(4-Cyanophenyldiazenyl)-1-methyl-2-phenyl-1H-indole (V)

This dye was obtained from 4-cyanoaniline and 1-methyl-2-phenyl-1H-indole. Yield: 74%, m.p.: 257–258, FT-IR (KBr) v_{max} (cm⁻¹): 3022 (aromatic C—H), 2928 (aliphatic C—H), 2222 (C \equiv N), 1469 (C=C), 1386 (N=N); ¹H NMR (DMSO-*d*₆): δ 8.55 (d, 1H, *J* = 7.68 Hz), 7.93 (d, 2H, *J* = 8.40 Hz), 7.78 (d, 2H, *J* = 8.30 Hz), 7.73 (d, 2H, *J* = 8.04 Hz) 7.67–7.60 (m, 4H), 7.46 (t, 1H, *J* = 7.18 Hz), 7.40 (t, 1H, *J* = 7.21 Hz), 3.85 (s, 3H, $-N--CH_3$); ¹³C NMR (DMSO-*d*₆): 156.53, 149.10, 137.87, 133.97, 133.12, 132.03, 130.04, 129.06, 128.69, 125.18, 124.52, 123.04, 122.34, 119.44, 118.13, 111.55, 110.44, 32.29; HRMS (*m*/*z*): found 337.1458 (calculated: 337.1453) for C₂₂H₁₇N⁴₄, [M–H]⁺.

3-(4-Nitrophenyldiazenyl)-1-methyl-2-phenyl-1H-indole (VI')

This dye was obtained from 4-nitroaniline and 1-methyl-2-phenyl-1H-indole. Yield: 70%, m.p.: 235–237, FT-IR (KBr) v_{max} (cm⁻¹): 3045 (aromatic C—H), 2940 (aliphatic C—H), 1512 (C=C), 1380 (N=N); ¹H NMR (DMSO-*d*₆): δ 8.55 (d, 1H, *J* = 7.55 Hz), 8.31 (d, 2H, *J* = 8.83 Hz), 7.85 (d, 2H, *J* = 8.84 Hz), 7.84–7.75 (m, 2H), 7.73 (d, 1H, *J* = 8.01 Hz), 7.70–7.63 (m, 3H), 7.45 (t, 1H, *J* = 7.29 Hz), 7.42 (t, 1H, *J* = 7.17 Hz), 3.90 (s, 3H, $-N--CH_3$); ¹³C NMR (DMSO*d*₆): 158.01, 149.70, 146.69, 137.96, 133.59, 132.07, 130.16, 128.95, 128.74, 125.48, 125.36, 124.75, 123.09, 122.35, 118.11, 111.66, 32.39; HRMS (*m*/*z*): found 357.1352 (calculated: 357.1352) for C₂₁H₁₇N₄O[±]₂, [M–H]⁺.

Results and discussions

Spectral characterizations

The phenylazoindole dyes were synthesized by coupling 2-phenylindole and 1-methyl-2-phenyl indole with aniline and 4-substituted diazotized aniline derivatives (Scheme 1). The structure of the synthesized dyes (I-VI and I'-VI') was confirmed by FT-IR, ¹H/¹³C NMR and HRMS. Five of these dyes (I, I', II', III and III') were also characterized by using single crystal X-ray diffraction techniques. Molecular structures of the synthesized dyes were given in Table 1.

The determination of azo-hydrazone tautomerism is the most interesting research field because both tautomeric structures have different technical, biological and photophysical properties [3]. Thus, it is necessary to determine the most tautomeric structure for all newly synthesized azo dyes. The stability of tautomers depends on environmental conditions such as solvent, acid/base and heat. The quantitative and qualitative evaluation of the azohydrazone tautomeric equilibria can be done by UV-vis and NMR Table 1Structures of dyes.



spectroscopy in solution. However, these methods have some disadvantages. In the case of UV-vis spectroscopy, equilibrium constant (K_T) cannot generally be obtained directly because the molar extinction coefficient of the individual tautomers cannot be determined, due to overlapping peaks of the two forms [29,30]. Also, ¹H NMR spectroscopy is not suitable for determination of azo-hydrazone tautomeric equilibria and equilibrium constant (K_T) . Because the equilibrium between azo and hydrazone tautomers is rapidly established on the NMR time scale [30,31]. However, ¹⁵N, ¹⁴N and ¹³C NMR chemical shift data can readily be employed to study quantitatively the azo-hydrazone tautomeric equilibrium [32–35]. Furthermore these methods are not employed for all azo dyes. Among the different methods, UV-vis and NMR spectroscopy are still the best methods for qualitative studies of tautomeric behavior in solutions. Also, the useful system for determination of the azo-hydrazone tautomerism is to use model compounds [16-22,36].

Hydrazide protons in hydrazone tautomer can easily be identified by the presence of one broad singlet in the ¹H NMR spectrum. Generally they are observed at ~14–15 ppm [35,37]. In this study, the ¹H NMR spectra of dyes (**I–VI**) showed the —NH peaks in the range of 11.65–12.70 ppm in DMSO- d_6 . Thus the observed values for —NH peaks clearly showed that the dyes **I–VI** can exist as azo form in DMSO. In addition, imine carbons could not observed in ¹³C NMR spectra for dyes (**I–VI**). Detailed spectral data are given in the Experimental section.

In addition to NMR results, to determination of the most tautomeric form of dyes (**I–VI**), the UV–vis absorption spectra of synthesized dyes in various solvents with different dielectric constants are evaluated and results are reported in Table 2. The absorption maxima (λ_{max}) values can be directly proportional to polarity of solvents and the electronic effect of the substituents in diazo part [38]. To investigate of solvatochromic behaviors of the dyes, the absorption spectra of phenylazoindole dyes (**I–VI**) were measured in various solvents at a concentration of approximately 2 × 10⁻⁵, and were compared with those of the corresponding model compounds (**I'–VI'**) containing the 1-methyl-2-phenylindole (Table 1).

The synthesized phenylazoindole dyes (I–VI) may be theoretically involved in azo-hydrazone tautomers (Scheme 2). Thus, the role of the azo-hydrazone tautomerism in relation to the visible absorption spectra and solvatochromic behavior of the dyes have been investigated. It is obtained that the absorption maxima of the dyes have correlations with the solvent polarities and small bathochromic shifts were observed with the increasing polarity of the solvents used. The visible absorption spectra of the prepared dyes showed one absorption maximum in all solvents used with the exception of the dyes **V** and **VI** in DMSO. It is known that two maxima are observed for compounds exhibiting azo-hydrazone tautomeric equilibria or anion.

In addition, when a comparison between λ_{max} values of the dyes (**I–VI**) and their corresponding model compounds (**I**–**VI**[']), the dyes are in favor of the predominantly azo form except **V** and **VI** in all solvents used. The small hypsochromic and bathochromic shifts in λ_{max} of the dyes in these solvents are due to solute–solvent interactions.

The effects of the substituents on the absorption maxima can also be found from Table 2. The introduction of the cyano and nitro groups in para position into the diazo component results in large bathochromic shifts in all solvents used (for dye **VI** λ_{max} = 65 nm in DMSO, λ_{max} = 51 nm in methanol, λ_{max} = 48 nm in acetic acid, λ_{max} = 52 nm in chloroform relative to λ_{max} of dye **I** in the same solvents). This bathochromic shift is attributed to the stronger electron-withdrawing character of nitro and cyano groups. The both groups enhance electron delocalization from indole to phenyldiazenyl part in the dye molecule.

The λ_{max} values of the dyes **V** and **VI** peaks at 431, 522 nm and 465, 600 nm showed respectively, which indicate the existence of both azo as well as hydrazone forms in DMSO. The peaks at 431 and 465 nm were attributed to the azo form because for their

Table 2						
Influences	of solvents an	d pH on	Amay (nm)) of dves	(I-IV) an	$d(\mathbf{I}' - \mathbf{V}\mathbf{I}')$

Compound number	DMSO		Methanol		Methanol + HCl	Methanol + KOH	Acetic acid		Chloroform		
	λ_{\max} (nm)	$\log \varepsilon^{b}$	λ_{\max} (nm)	$\log \varepsilon^{b}$	λ_{\max} (nm)	λ_{\max} (nm)	λ_{\max} (nm)	$\log \varepsilon^{b}$	λ_{\max} (nm)	$\log \varepsilon^{b}$	
I	400	4.76	394	4.61	461	393	393	4.69	390	4.66	
II	405	4.75	396	4.70	401,493(s) ^a	396	396	4.78	394	4.72	
Ш	401	4.73	393	4.76	400,472(s) ^a	393	394	4.72	391	4.76	
IV	412	4.75	400	4.59	410,451(s) ^a	400	400	4.74	398	4.75	
V	431,522(s) ^a	4.76	421	4.79	427	422	419	4.73	419	4.75	
VI	465,600	4.78	445	4.76	451	449,552(s) ^a	441	4.79	442	4.78	
ľ	392	4.70	386	4.64	456	384	386	4.70	387	4.78	
11′	397	4.73	390	4.74	493	390	391	4.67	393	4.72	
III′	401	4.74	393	4.71	473	395	387	4.72	392	4.73	
IV′	402	4.78	395	4.72	397,451(s) ^a	394	396	4.79	395	4.75	
V′	422	4.78	414	4.65	432	414	414	4.67	415	4.76	
VI′	454	4.70	436	4.78	441	435	434	4.75	441	4.75	

^a s: shoulder.

^b ε in cm⁻¹ M⁻¹.

model compounds (**V**' and **VI**') was observed similar λ_{max} values 422 and 454 nm which exist only azo form.

To provide conclusive evidence for the tautomeric structure of the compounds, the effects of acid and base on their absorption spectra were also investigated. For this purpose, the spectra of the dyes were recorded in acidic and basic media. The protonation and deprotonation of the dyes can lead to the common cation and anion (Scheme 2). It was observed that the absorption curves of the dves were not sensitive to base, except dye VI when various amounts of 0.1 M KOH was added to their methanolic solutions (Table 2). This result indicates that dyes **I**–**V** exist in one tautomeric form in alkaline media and there are no dissociated species. As shown in Table 2, when introduction of strong electron withdrawing group such as nitro in diazocomponent, a new shoulder was appeared at longer wavelength (552 nm) with the addition of 0.1 M KOH to methanolic solution of the dve **VI**. This indicated that this dve exists in a partly dissociated state in methanolic KOH solutions.

The λ_{max} values of some dyes showed large bathochromic shifts when various amounts of 0.1 M HCl were added to their methanolic solutions except dyes **V**, **VI**, **V**' and **VI**' containing the electronwithdrawing substituents (Table 2). It showed that the dyes observed at longer wavelengths exist in azonium tautomer, which contains a delocalized positive charge (Scheme 2).

Theoretical study

The most relevant geometrical parameters of azo and hydrazone forms of the dyes **I–VI** and model compounds (dyes **I'–VI'**), which can be only in the azo form are given in Table S1 (Supporting Information, page S2). For the dyes **I–IV**, the N—N bond lengths are between 1.265 and 1.270 Å, in accordance with their model compounds **I'–IV**' in the azo form and between 1.316 and 1.329 Å in the hydrazone form. However, the X-ray data show that they are double bonds which characterize the azo form.

The values of N1–C8 and adjacent N2–C7 single bonds for the azo form are compatible with the X-ray single-crystal analyses results, which show that the dyes **I**, **I'**, **II'**, **III** and **III'** are in the azo form Fig. 2. However, the results show that the optimized structures of the molecules are all nearly planar. There is no X-ray structures for the dyes **II**, **IV**–**IV'**, **V**–**V'**, **VI**–**VI'** to compare, we shall consider the stabilities of the azo and hydrazone forms of the dyes. On the other hand, it is seen that there is no effects of the electron-withdrawing (**IV**–**IV'**, **V**–**V'** and **VI**–**VI'**) and electron-donor (**III–III'** and **II–II'**) substituents at para position of the phenyl rings on the geometrical structures with respect to dyes **I**–**I**'.

To compare the stabilities of the azo and hydrazone forms of the dyes, each form of the dyes are optimized in gas-phase and in different solvents having different dielectric constants (ε) such as



Fig. 2. Molecular structures of the dyes I, I', II', III and III'. Thermal ellipsoids are drawn at the 40% probability level.

DMSO (ε = 46.45 D), methanol (ε = 33.1 D), acetic acid (ε = 6.17 D) and chloroform (ε = 4.81 D). The calculated relative total energies (ΔE_t) and Gibbs free energies (ΔG) and enthalpies (ΔH) of dyes **I–VI** in their azo and hydrazone forms (they are given in Table S2, Supporting Information, page S3) for gas phase and for different solvents. On the basis of these results, the azo tautomer is more stable than hydrazone tautomer for the dyes **I–VI** in gas phase and in solution. However, the stability of the azo tautomer slightly increases from DMSO to chloroform with decreasing dielectric constant.

The energy analyses for stabilities of the dyes show that the azo form is more stable than the hydrazone form both in gas phase and solution [17]. In our continuation study, the electronic spectra of the compounds in azo and hydrazone forms were also obtained in the framework of TD-DFT calculations with B3LYP using 6-311+g(d,p) basis set to support the assignment of absorption bands for azo and hydrazone forms. In these calculations, different solvents were used to evaluate the solvent effects on maximum absorption wavelengths for each molecule. For azo and hydrazone forms of dyes **I–VI** and their related model compounds **I'–VI'**, the maximum wavelengths (λ_{max}), oscillator strengths (f) and major contributions of the calculated transitions in different solutions are summarized in Table S3 (Supporting Information, pages S4 and S5).

The obtained results indicate that the calculated λ_{max} values are higher than the corresponding values in the experimental data. The differences between calculated and experimental values change from 5 nm for the azo tautomeric form of dye I to 65 nm for dye VI' in methanol in relative to experimental data. However, the absorption bands for dyes I–VI (azo form) and dyes I'–VI' arise excitations from HOMO to LUMO in solvents used.

On the other hand, it is obtained that the calculated λ_{max} values and the corresponding oscillator strengths values did not change significantly in all the employed solvents and did not correlate with the polarity of the solvent for each dye. As the polarity increases from chloroform to DMSO, the biggest differences are 23 nm for azo form of dye **VI** and 13 nm for dye **VI**' according to the experimental results (Table 2).

The effects of the substituents on the absorption maxima could also be found in Table 2. It is seen that the λ_{max} values of the azo tautomeric form showed a shift to longer wavelengths for the dyes **V**, **VI**, **V'**, **VI'** including the electron-withdrawing substituents and no significant changes for dyes **II**, **II'**, **III**, **III'** as compared to the dyes **I** and **I'**. The obtained results are compatible with the experimental and theoretical data.

Conclusions

Six tautomeric phenylazo indole dyes (I–VI) and their six corresponding model compounds (I'–VI') which exist only in azo tautomeric form were synthesized and characterized. X-ray single-crystal analyses of dyes I, I', II', III and III' show that these dyes crystallize in azo form in solid state. However, the used spectroscopy techniques analysis confirm that the azo form is predominant for synthesized dyes (I–V) in all solvent used. The experimental data are compared with theoretical values and it was found that the calculation results are in very good agreement with the experimental data.

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Appendix A. Supplementary material

The detailed spectroscopic data (copies of ¹H/¹³C NMR and UVvis spectra for all new compounds) including crystallographic data (CIF) of all new compounds are available. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic data Centre as the supplementary publication Nos. CCDC-988708 (for I), CCDC-990250 (for I'), CCDC-990618 (for II'), CCDC-990613 (for III), CCDC-990904 (for III'). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.09.082.

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