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# Phenylazoindole dyes 2: The molecular structure characterizations of new phenylazo indoles derived from 1,2-dimethylindole

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# $A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

In this study, five new phenylazo indoles derived from 1,2-dimethylindole were synthesized and characterized to evaluate the substituent effects on the molecular structures and absorption spectra. Theoretical calculations were carried out by density functional theory. The experimental and theoretical results are compared. X-ray single-crystal diffraction analyses reveal that the dyes have similar planar molecular conformation between azo and aromatic/heteroaromatic ring units but dissimilar crystal packing. The analysis of the electronic spectra showed that the electron-withdrawing groups (-CI and -CN) were more effective than the electron-donating groups ( $-CH_3$  and  $-OCH_3$ ). Dyes containing electron-donating groups do not show significant changes relative to the parent dye, whereas the absorption maxima move to longer wavelengths for dyes containing electron-withdrawing groups . In addition, the absorption maxima exhibit the little bathochromic shifts for each dye with the increasing dielectric constants of the solvents.

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# 1. Introduction

It is well known that azo dyes have one or more -N=Ngroups, which link two aromatic/heteroaromatic rings and are the most widely used class of dyes [1–3]. In recent years, much attention has been directed to the investigations of the chemical and physical properties of azo dyes, due to their biological and physicochemical properties [1–9] as well as their potential wide applications in many other fields [10–14].

Although there is an extensive literature on azo dyes, it is very important to synthesize and characterize new azo dyes experimentally and also theoretically using the computational method to provide guidance for further studies. The dyes based on heterocyclic coupling components such as indoles are commercially important azo dyes [1]. In earlier studies [15,16], we have reported the tautomeric properties of some phenylazoindole dyes and X-ray crystal structure of 3-phenyldiazenyl1,2-dimethyl-1*H*-indole (dye 1). In our ongoing study, the syntheses of a new series, phenylazo-1,2-dimethylindole, containing the electron-withdrawing (-CN and -Cl) and electron-donating  $(-CH_3 \text{ and } -OCH_3)$  groups at para position of the phenyl ring are reported. The effects of the substituent groups on the groundstate geometries, energies of molecular orbitals and absorption wavelengths are investigated by using the spectroscopic and computational techniques. This study is important since it provides the first syntheses and characterizations of the five new azo dyes by using the spectroscopic techniques. In addition, the crystal structure of each dye was also obtained. In calculations, the density functional theory (DFT) method was employed to obtain the ground state geometries of all dves and timedependent DFT (TD-DFT) was used to study the absorption spectra in gas phase and in solution. According to the experimental and theoretical results, the discussion of the influences produced by the substituent groups and by the different solvents on the absorption wavelenghts, the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO) and also molecular electrostatic maps (MEP) are given with respect to our reference compound (dye 1, Fig. 1).







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Fig. 1. Synthetic pathway and structure of compounds.

### 2. Experimental

# 2.1. Material and methods

The chemicals used in the syntheses of all compounds were from the Aldrich Chemical Company and used without further purification. The solvents were used of spectroscopic grade. IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr ( $\nu$ , are in cm<sup>-1</sup>). H NMR spectra were recorded on a Bruker-Spectrospin Avance DPX 300 Ultra-Shield in DMSO-d<sub>6</sub>. Chemical shifts are expressed in  $\delta$  units (ppm). Ultraviolet–visible (UV–vis) absorption spectra were recorded on Analytik Jena Specord 200 spectrophotometer at the wavelength of maximum absorption ( $\lambda_{max}$ , in nm) in the solvents specified. Mass spectra were recorded on a Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments; in *m*/*z* (rel. %). The X-ray data were recorded in the Department of Chemistry, Atatürk University, Erzurum, Turkey.

#### 2.2. Preparation of dyes (1–5)

Various carbocyclic amines can be diazotized with HCl and NaNO<sub>2</sub>. A typical procedure of diazotizing and coupling is described below using aniline and 1,2-dimethylindole; all other compounds were prepared in a similar manner. The yields of the dyes are in the range of 76–90%. The obtained compounds were purified by crystallization using ethanol by slow evaporation in several days, and then analyzed.

# 2.2.1. Preparation of (E)-3-phenyldiazenyl-1,2-dimethyl-1H-indole (1)

Aniline (0.18 mL, 2.0 mmol) was dissolved in concentrated HCl (1.5 mL, % 36 w/w) and water (4.0 mL). The solution was cooled in an ice-salt bath and a cold solution of NaNO<sub>2</sub> (0.15 g, 2 mmol) in water (3.0 mL) was added dropwise with stirring. The mixture was stirred for an additional 1 h at 273 K. Excess nitrous acid was destroyed by the addition of urea. The resulting diazonium salt was cooled in a salt/ice mixture. 1,2-dimethylindole (0.29 g, 2.0 mmol) was dissolved in a mixture of acetic acid and propionic acid solution (3.0: 1.8 mL) and cooled in an ice bath. Then, cold diazonium solution was added to this cooled solution by stirring in a dropwise manner. The solution was stirred at 273-278 K for 1 h. The pH of the reaction mixture was maintained at 4–6 by the simultaneous addition of saturated sodium carbonate solution. The mixture was stirred for a further 1 h at room temperature. The resulting solid was filtered, washed with cold water, and then dried. Recrystallization from ethanol gave yellow crystals (0.425 g, 85% yield; m.p: 125 °C) FT-IR (KBr) vmax: 3055 (aromatic C-H), 2915 (aliphatic C-H), 1534, 1476, 1446 (C=C), 1387 (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.39 (dd, 1H,  $J_1$  = 7.80 Hz,  $J_2$  = 1.11 Hz), 7.82 (dd, 2H,  $J_1$  = 8.10 Hz,  $J_2 = 1.13$  Hz), 7.58 (d, 1H,  $J_1 = 7.59$  Hz), 7.51 (t, 2H,  $J_1 = 8.01$  Hz), 7.38 (t, 1H,  $J_1$  = 7.28 Hz), 7.29 (td, 1H,  $J_1$  = 7.25 Hz,  $J_2$  = 1.33 Hz), 7.25 (td, 1H,  $J_1 = 7.37$  Hz,  $J_2 = 1.05$  Hz), 3.74 (s, 3H,  $-NCH_3$ ), 2.82 (s, 3H,  $-CH_3$ ), HRMS (M<sup>+</sup>) calcd for  $C_{16}H_{16}N_3$  250.1344; found, 250.1343.

# 2.2.2. Preparation of (E)-3-(4-Methylphenyldiazenyl)-1,2-dimethyl-1H-indole (**2**)

The dye was obtained from p-toluidine and 1,2-dimethylindole as orange crystals (0.465 g, 88% yield; m.p: 145 °C) FT-IR (KBr)  $v_{max}$ : 3024 (aromatic C–H), 2918 (aliphatic C–H), 1598, 1535, 1472, 1448 (C=C), 1385 (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.40 (d, 1H,  $J_1$  = 8.04 Hz), 7.78 (d, 2H,  $J_1$  = 8.87 Hz), 7.55 (d, 1H,  $J_1$  = 7.90 Hz), 7.30–7.20 (m, 2H), 7.05 (d, 2H,  $J_1$  = 8.89 Hz), 3.70 (s, 3H, –NCH<sub>3</sub>), 2.60 (s, 3H, –CH<sub>3</sub>), 2.38 (s, 3H, –CH<sub>3</sub>), HRMS (M<sup>+</sup>) calcd for C<sub>17</sub>H<sub>18</sub>N<sub>3</sub> 264.1501; found, 264.1507.

# 2.2.3. Preparation of (E)-3-(4-Methoxyphenyldiazenyl)-1,2dimethyl-1H-indole (**3**)

The dye was obtained from p-anisidine and 1,2-dimethylindole as yellow crystals (0.504 g, 90% yield; m.p: 105 °C) FT-IR (KBr)  $v_{max}$ : 3050 (aromatic C–H), 2932–2833 (aliphatic C–H), 1598, 1577, 1537, 1495, 1455 (C=C), 1387 (N=N), 1245 (C–O) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.40 (d, 1H,  $J_1$  = 7.25 Hz), 7.70 (d, 2H,  $J_1$  = 8.21 Hz), 7.56 (d, 1H,  $J_1$  = 7.85 Hz), 7.35 (d, 2H,  $J_1$  = 8.18 Hz), 7.30–7.20 (m, 2H), 3.85 (s, 3H, –OCH<sub>3</sub>), 3.78 (s, 3H, –NCH<sub>3</sub>), 2.80 (s, 3H, –CH<sub>3</sub>), HRMS (M<sup>+</sup>) calcd for C<sub>17</sub>H<sub>18</sub>N<sub>3</sub>O 280.1455; found, 280.1453.

### 2.2.4. Preparation of (E)-3-(4-Chlorophenyldiazenyl)-1,2-dimethyl-1H-indole (**4**)

The dye was obtained from p-chloroaniline and 1,2dimethylindole as yellow crystals (0.436 g, 82% yield; m.p: 137 °C) FT-IR (KBr)  $v_{max}$ : 3047 (aromatic C–H), 2931 (aliphatic C– H), 1531, 1473, 1451, 1404 (C=C), 1380 (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.45 (d, 1H,  $J_1$  = 7.18 Hz), 7.89 (d, 2H,  $J_1$  = 8.68 Hz), 7.64 (d, 1H,  $J_1$  = 8.90 Hz), 7.62 (d, 2H,  $J_1$  = 8.71 Hz), 7.37–7.28 (m, 2H), 3.85 (s, 3H, –NCH<sub>3</sub>), 2.82 (s, 3H, –CH<sub>3</sub>), HRMS (M<sup>+</sup>) calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>CI 284.0955; found, 284.0955.

# 2.2.5. Preparation of (E)-3-(4-Cyanophenyldiazenyl)-1,2-dimethyl-1H-indole (**5**)

The dye was obtained from p-aminobenzonitrile and 1,2dimethylindole as brown crystals (0.418 g, 76% yield; m.p: 152 °C) FT-IR (KBr)  $v_{max}$ : 3050 (aromatic C–H), 2910 (aliphatic C–H), 2224 (C $\equiv$ N), 1596, 1529, 1474, 1409 (C $\equiv$ C), 1394 (N=N) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.41 (dd, 1H,  $J_1$  = 8.13 Hz,  $J_2$  = 1.59 Hz), 7.94 (m, 4H), 7.60 (d, 1H,  $J_1$  = 7.45 Hz), 7.35 (td, 1H,  $J_1$  = 7.26 Hz,  $J_2$  = 1.42 Hz), 7.25 (td, 1H,  $J_1$  = 7.25 Hz,  $J_2$  = 1.12 Hz), 3.70 (s, 3H, –NCH<sub>3</sub>), 2.60 (s, 3H, – CH<sub>3</sub>), HRMS (M<sup>+</sup>) calcd for C<sub>17</sub>H<sub>15</sub>N<sub>4</sub> 275.1297; found, 275.1295.

# 2.3. Computational study

The geometries of all the compounds (dyes 1-5) has been fully optimized in the ground state at the B3LYP/6-311+G(p,d)

computational level [17–19]. The integral equation formalism of the polarizable continium model (PCM) was employed [20,21]. The vibrational frequencies were calculated at the same theoretical level to confirm that all optimized ground configurations had no imaginary frequencies and the ground-state minima were on potential energy surfaces. Absorption spectra were computed as vertical electronic excitations from the ground-state minima by using the time-dependent density functional theory (TD-DFT) [22]. All calculations were performed with the Gaussian 09 program [23].

# 2.4. Crystallography

X-ray diffraction data of the azo dyes 2-5 were collected for comparison of the structural results with the corresponding ones obtained from the theoretical calculations. Diffraction data collections were performed on a Rigaku R-AXIS RAPID-S diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at T = 294 K. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc., 2005) software [24]. The structures were analyzed using a combination of direct and difference Fourier methods provided by SHELXS97 [25] and were refined as full-matrix least squares against  $F^2$  using all data by SHELXL97 [25] computer programs; all nonhydrogen atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.93 (for aromatic CH) and 0.96 Å (for methyl groups) from the parent C atoms; a riding model was used during the refinement processes and the U<sub>iso</sub>(H) values were constrained to be  $xU_{eq}$  (carrier atom), where x = 1.5 for methyl H, and x = 1.2 for aromatic H atoms. The final difference Fourier maps showed no peaks of chemical significance. Crystal data and details of the structure determination for the compounds are summarized in Table 1.

# 3. Results and discussion

#### 3.1. Description of the crystal structures

The single-crystal X-ray structural determinations of dye molecules are of great significance because they reveal their molecular conformations, packing fashions and supramolecular interactions, which will help to understand the interactions between dyes and fibers, the coloring mechanism and other related technical performance [26–28].

The asymmetric units of dyes 2, 4 and 5 contain only one molecule (Fig. 2(a),(c) and (d)), while the asymmetric unit of dye **3** contains two crystallographically independent molecules (Fig. 2(b)). Selected bond lengths and angles together with the selected torsion angles are given in Table 2. An examination of the deviations from the least-square mean planes through the individual rings showed that all of the rings are planar. The indole ring systems were planar with dihedral angles of  $0.76(13)^{\circ}$  (for dye **2**), 3.19(15)° and 0.72(15)° (for dye **3**), 2.54(13)° (for dye **4**) and  $1.04(18)^{\circ}$  (for dye 5) between rings A (N1/C1-C3/C8) and B (C3-C8) (for dyes 2, 3, 4 and 5) and between rings A' (N1'/C1'-C3'/C8') and B' (C3'-C8') (for dye **3**). In the closely related compounds, 3-(4chlorophenyldiazenyl)-1-methyl-2-phenyl-1H-indole 6 [29], N-{4-[(2-phenyl-1*H*-indol-3-yl)-diazenyl]-phenyl}acetamide **7** [30], ethyl[2-(2-phenyl-1H-indol-3-yldiazenyl)-1,3-thiazol-4-yl] acetate 8 [31], 1,2-dimethyl-3-(pyridin-3-yldiazenyl)-1H-indole 9 [32] and 1,2-dimethyl-3-(5-methylisoxazol-3- yldiazenyl)-1H-indole 10 [33], the observed A/B and A'/B' dihedral angles were  $1.56(11)^{\circ}$  and 0.77(12)° in 6 1.63(14)° in 7, 0.99(10) in 8, 2.71(7)° in 9 and 0.45(11)° in 10. The orientations of the phenyl rings C (C11-C16) and C'(C11'-C16') with respect to the planar indole ring systems might be described by the dihedral angles of  $12.97(7)^{\circ}$  (for dye **2**), 15.80(11)° and 19.50(13)° (for dye **3**), 11.83(10)° (for dye **4**), and 4.18(8)° (for dye 5). The partial packing diagrams are shown in Fig. 3(a)–(d), for dyes 2, 3, 4 and 5, respectively. The bond lengths of azo units (N2–N3) are in the range of 1.272(4)–1.285(5)Å corresponding to the double-bond character.

In the crystal packing of azo **2–5** dyes,  $\pi...\pi$  stacking interactions are found between the phenyl rings and the indole rings of neighboring molecules with the centroid–centroid separations of 3.626(2)- 3.852(2) Å. There also exist weak C–H... $\pi$  interactions in dyes **2–5** (Table 3). In dye **3**, there are no classical intermolecular hydrogen bonds but C–H...O short contacts (Table 3) describe a cyclic tetramer (Fig. 3(b)).

#### 3.2. Geometric parameters

The optimized structure parameters by DFT method with B3LYP functional are listed in Table 2, which are in accordance with the

#### Table 1

Crystallographic details for dyes 2, 3, 4 and 5.

Dyes	2	3	4	5
Chemical formula	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub>	$C_{34}H_{34}N_6O_2$	C <sub>16</sub> H <sub>14</sub> N <sub>3</sub> Cl	C <sub>17</sub> H <sub>17</sub> N <sub>4</sub>
FW/g mol <sup>-1</sup>	263.34	558.67	591.9	274.32
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c	P -1	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a/Å	7.3848(3)	7.267(5)	7.3264(3)	8.3501(2)
b/Å	15.2260 (5)	10.695(5)	15.2210(4)	12.8232(3)
c/Å	12.8781(4)	20.349(4)	12.8722(3)	14.2205(4)
$\alpha / ^{\circ}$	90	98.943(5)	90	90
$\beta I^{\circ}$	93.31(3)	90.630(5)	92.21(2)	102.674(2)
$\gamma I^{\circ}$	90	106.469(5)	90	90
V/Å <sup>3</sup>	1445.61(10)	1495.7(13)	1434.38(8)	1485.56(7)
Ζ	4	2	4	4
$\rho_{\rm calc} {\rm mg}/{\rm mm}^3$	1.210	1.241	1.31	1.227
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.73	0.80	0.259	0.076
F(000)	560	592	592	576
Crystal size/mm <sup>3</sup>	$0.35\times0.22\times0.20$	$0.30\times0.25\times0.15$	$0.24\times0.19\times0.12$	$0.35 \times 0.20 \times 0.15$
$2\Theta$ range for data collection	4.14–52.84°	4.20–52.84°	2.7–54.6°	4.32-53.42°
Reflections collected	29717	31015	24551	30583
Independent reflections	2960[R(int) = 0.076]	6106[R(int) = 0.087]	2984[R(int) = 0.103]	3071[R(int) = 0.084]
Data/restraints/parameters	2960/0/184	6106/0/385	2984/0/184	3071/0/192
Goodness-of-fit on F <sup>2</sup>	0.981	0.996	1.19	1.051
Final R indexes $[I \ge 2\sigma (I)]$	$R_1 = 0.0752$ , w $R_2 = 0.2053$	$R_1 = 0.0809$ , w $R_2 = 0.1868$	$R_1 = 0.093$ , w $R_2 = 0.232$	$R_1 = 0.0715$ , w $R_2 = 0.1820$
Largest diff. peak/hole/e Å <sup>-3</sup>	0.202/-0.290	0.167/-0.207	0.366/0.552	0.197/-0.187



Fig. 2. An ORTEP [38] drawing with the atom-numbering scheme for (a) dye2, (b) dye3, (c) dye4, (d) dye5.

atom numbering scheme given in Fig. 2, and they are compared with experimental results.

N<sub>2</sub>=N<sub>3</sub> bond lengths are identified by X-ray between 1.272 and 1.184 Å and by B3LYP between 1.265 and 1.269 Å. All of the computed N<sub>2</sub>=N<sub>3</sub> bonds are slightly shorter than the experimental ones. The dyes exist in azo form because they have no tautomeric hydrogen. Kelemen et al. reported that N=N bond is between 1.20 and 1.28 Å in azo tautomers [34]. Geometric parameters for these azo dyes agree with the corresponding values in our previously reported studies of indole azo dyes [32,33]. We have identified N= N bond length for 1,2-dimethyl-3-(pyridin-3-yldiazenyl)-1H-indole [32] by X-ray as 1.276 Å and by B3LYP as 1.272 Å and for 1,2dimethyl-3-(5-methylisoxazol-3-yldiazenyl)-1H-indole [33] by Xray as 1.281 Å and B3LYP as 1.269 Å. The calculated bond lengths of the N3-C1 bonds in dyes are estimated in the range of 1.374-1.418 Å and they are shorter than the experimental values (1.423-1.440 Å). The errors of bond lengths between the calculated results and the X-ray data are less than 0.032 Å, which corresponds to the C11–C12 bond length for dye 5. It is known that large deviations from experimental C-H bond lengths may arises from the low scattering factors of hydrogen atoms in the X-ray diffraction experiments. Therefore the discussion of C-H bond length was not given in here.

The optimized structures of these molecules are nearly planar. The calculated C1-N2-N3-C11 values of dyes are  $180^{\circ}$ , and the corresponding experimental values lie between 173 and  $180^{\circ}$ . The highest difference between X-ray and calculated angular values corresponds to the N2-N3-C11 bond angle for dye **3** as  $2.7^{\circ}$ .

#### 3.3. Spectral characterizations

The theoretical and experimental absorption wavelenghts are obtained in various solvents having different dielectric constants ( $\varepsilon$ ) such as DMSO ( $\varepsilon$  = 46.45 Debye), acetic acid ( $\varepsilon$  = 6.17 Debye) and chloroform ( $\epsilon$  = 4.81 Debye). The absorption spectra of dyes 1–5 were recorded over the  $\lambda$  range of (300–700) nm using a variety of solvents in concentrations  $10^{-6}$ – $10^{-8}$  M. In calculations, the absorption spectra of dyes were calculated at the optimized structure of the ground state in each solvents using the PCM model linked to TD-DFT (B3LYP) with the 6-311+G(d,p). The obtained results are given in Table 4. As can be seen in Table 4, the dves have strong single absorption bands, which are assigned to the  $n-\pi^*$  transitions from the indole ring to the azo unit in compounds in all solvents. However, for dyes (1–3) in acetic acid the additional strong bands are observed at 437, 448 and 466 nm, which can be assigned to the protonated species for dyes 1, 2 and 3, respectively. Protonation takes place on the  $\beta$ -nitrogen atom of the azo group (Fig. 4), and as a result a migration of electrons occurs from the electron-rich phenyl ring to the azo group and the absorption band is seen at a longer wavelength. For dyes **4** and **5**, the donor properties of  $\beta$ -nitrogen atom of the azo group is decreased, because of the electronwithdrawing groups located at the para position of the phenyl ring, and consequently an additional second band corresponding to the protonation is not observed. The calculated absorption bands at 387 nm with (oscillator strength *f*) f = 0.92, 389 nm with f = 1.00and 396 nm with f = 1.05 are assigned to the first bands at 385, 385 and 384 nm for dyes 1–3, respectively.

#### Table 2

Selected bond lengths (Å) and angles (°) with the selected torsion angles (°) for dyes 1–5. The calculated values are for gas phase.

	1		2		3			4		5	
	- Evn <sup>a</sup>	Calc	- Evn	Calc	Fyp		Calc	Evp	Calc	Evn	Calc
	слр.	Calc.	LAP.	calc.	<u>Ехр.</u>		calc.	LAP.	calc.	LAP.	calc.
					Unprimed	Primed					
Bond lengths											
01 – C14					1.370(5)	1.376(5)	1.363				
01 – C17					1.428(5)	1.418(5)	1.421				
N1 – C2	1.363 (3)	1.373	1.366 (4)	1.374	1.366(5)	1.361(5)	1.375	1.360(5)	1.371	1.351(3)	1.368
N1 – C3	1.388 (3)	1.394	1.386(4)	1.394	1.375(6)	1.376(6)	1.393	1.388(6)	1.395	1.389(3)	1.397
N1 – C9	1.457 (3)	1.451	1.458(4)	1.451	1.465(5)	1.455(5)	1.451	1.477(6)	1.452	1.456(3)	1.453
N2 – N3	1.279 (3)	1.265	1.272(4)	1.265	1.284(5)	1.273(4)	1.265	1.275(5)	1.266	1.275(3)	1.269
N2 – C1	1.382 (3)	1.376	1.382(4)	1.377	1.384(5) 1.382(5)	1.378	1.313(7)	1.374	1.374(3	8) 1.369	
N3 – C11	1.429 (3)	1.418	1.437(4)	1.416	1.434(5)	1.423(5)	1.413	1.433(6)	1.374	1.440(3)	1.413
N4 – C17										1.133(4)	1.156
C1 – C2	1.390 (4)	1.396	1.379(4)	1.394	1.383(6)	1.383(6)	1.394	1.415(6)	1.396	1.394(4)	1.399
C1 – C8	1.442 (4)	1.449	1.442(5)	1.449	1.439(6)	1.437(6)	1.449	1.458(7)	1.450	1.434(3)	1.450
C2 - C10	1.482 (4)	1.489	1.478(4)	1.489	1.494(6)	1.481(6)	1.489	1.496(6)	1.490	1.478(3)	1.489
C3 – C4	1.382 (4)	1.394	1.389(5)	1.394	1.398(6)	1.387(6)	1.394	1.421(5)	1.393	1.394(4)	1.393
C3 – C8	1.415 (3)	1.415	1.410(4)	1.416	1.410(6)	1.406(6)	1.416	1.403(5)	1.415	1.408(4)	1.414
C5 - C6	1.384 (4)	1.403	1.384(5)	1.404	1.390(7)	1.374(7)	1.404	1,404(6)	1.403	1.395(5)	1.403
(6 - C7)	1 378 (4)	1 391	1 375(5)	1 391	1 366(6)	1 393(6)	1 391	1 390(5)	1 391	1.387(4)	1 392
C7 - C8	1 393 (4)	1 401	1 396(4)	1 401	1 393(6)	1 391(6)	1 401	1421(7)	1 400	1400(4)	1 400
$C_{11} = C_{12}$	1 397 (4)	1 400	1 377(5)	1 399	1 391(6)	1 388(5)	1 408	1 393(6)	1 400	1371(4)	1 402
$C_{11} = C_{16}$	1.337(1) 1.387(4)	1.100	1 393(5)	1.555	1.377(6)	1.384(5)	1 396	1 336(5)	1.100	1.374(4)	1.102
C12 - C13	1381 (4)	1 302	1 389(5)	1 302	1.377(0)	1.304(5)	1 3 9 1	1.350(5)	1 301	1.374(4) 1.367(4)	1 3 8 7
C12 = C13	1381 (5)	1 30/	1.303(5) 1.372(5)	1 307	1.304(6)	1.372(0)	1,001	1.300(0)	1 301	1.307(4) 1.381(4)	1,507
C14 = C14	1.301 (5)	1 209	1.372(3) 1.299(5)	1,557	1.275(6)	1.369(6)	1,405	1.375(0) 1.426(5)	1,351	1.301(4) 1.270(4)	1,405
C14 - C13	1.360 (3)	1.556	1.566(5)	1.404	1.575(0)	1.509(0)	1.557	1.420(3)	1.555	1.379(4)	1.407
C14 - C17			1.508(5)	1.509					1 760	1.440(4)	1.429
CI4-CII Dand angles									1.760		
Bona angles	100.2 (2)	100.2	100 4(2)	100.2	100 1(4)	100.0(4)	100.2	100.0(4)	100.2	100 4(2)	100.4
C2-N1-C3	109.2 (2)	109.2	109.4(3)	109.2	109.1(4)	109.9(4)	109.2	109.8(4)	109.3	109.4(2)	109.4
CI-N2-N3	113.8 (2)	115.9	113.5(3)	115.9	114.4(4)	113.6(4)	115.8	115.4(4)	116.0	114.6(2)	116.0
N2-N3-C11	112.7 (2)	114.9	113.4(3)	114.9	112.4(4)	113.7(4)	115.1	114.8(3)	114.7	112.4(2)	114.5
C2-C1-C8	107.5 (2)	107.5	108.2(3)	107.5	107.4(4)	107.6(4)	107.5	106.0(4)	107.5	107.3(2)	107.5
N2 - C1 - C2	120.5 (2)	120.3	120.2(3)	120.4	120.3(5)	120.3(4)	120.4	121.4(4)	120.3	119.5(2)	120.3
N2-C1-C8	132.0 (2)	132.1	131.5(3)	132.1	132.3(4)	132.0(4)	132.1	132.5(4)	132.2	133.2(3)	132.3
N1-C2-C1	109.2 (2)	108.9	108.7(3)	109.0	109.1(4)	108.6(4)	109.0	109.1(4)	109.0	109.1(2)	108.9
N1-C3-C8	108.5 (2)	108.4	108.4(3)	108.4	108.6(4)	108.0(4)	108.4	108.5(4)	108.4	108.1(2)	108.4
N1-C3-C4	129.5 (3)	129.1	130.1(3)	129.1	129.5(5)	130.1(5)	129.1	127.9(4)	129.1	128.3(3)	129.0
C7–C8–C1	135.8 (2)	135.1	135.8(3)	135.1	136.0(4)	135.3(4)	135.1	133.8(4)	135.1	135.9(3)	135.1
C7–C8–C3	118.6 (2)	118.9	118.9(3)	118.9	118.3(5)	118.8(4)	118.9	119.3(4)	119.0	118.1(3)	119.1
C1-C8-C3	105.6 (2)	105.97	105.3(3)	105.9	105.7(4)	105.9(4)	105.9	106.5(4)	105.9	106.0(2)	105.8
N3-C11-C12	115.2 (3)	115.6	115.1(3)	115.9	115.9(4)	116.1(4)	116.1	114.3(5)	115.8	115.3(3)	115.7
N3-C11-C16	125.3 (3)	125.0	125.8(3)	125.3	125.2(4)	125.0(4)	125.3	125.2(4)	125.1	125.4(3)	125.1
C12-C11-C16	119.4 (3)	119.4	119.1(3)	118.8	118.8(4)	118.7(4)	118.6	120.3(4)	119.1	119.3(3)	119.2
Torsion											
C1-N2-N3-C11	-179.9(1)	180.0	176.6(2)	-179.8	178.2(3)	175.1(3)	-180.0	173.0(3)	180.0	179.1(2)	180.0
N2-N3-C11-C12	166.1 (2)	180.0	174.1(3)	-178.6	-10.7(6)	-16.2(6)	0.0	174.9(3)	180.0	178.2(2)	-180.0
N2-N3-C11-C16	-15.8 (4)	0.0	-8.5 (5)	1.4	170.9(3)	168.2(4)	-179.9	0.0	0.0	-1.6(4)	0.0
N3-N2-C1-C2	178.9 (2)	180.0	179.9(3)	-179.7	179.2(4)	-177.6(4)	-180.0	177.5(4)	180.0	178.0(2)	-180.0
N3-N2-C1-C8	-1.8(4)	0.0	-4.3 (5)	0.3	-4.7(6)	-3.1(6)	0.0	-7.0(3)	0.0	-1.1(4)	0.0
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<sup>a</sup> Ref. [15].

On the other hand, the absorption maxima exhibit the little bathochromic shifts for each dye by increasing the dielectric constants. For dye **1**, the biggest change is 7 nm in DMSO with respect to the value in chloroform. Similar trends were seen for dyes **2** and **3** with the value of 5 nm and for dyes **4** and **5** with the value of 7 nm. According to these findings, no significant solvent effects on the absorption maxima for dyes **1**–**5** were observed experimentally. The results of theoretical calculations are in accordance with these experimental results. Thus, it can be said that any change in the molecular structures of these dyes is not observed on different application environments. These obtained results are important for using of dyes in application process in different media.

The effects of the substituents on the absorption maxima could also be found from Table 4. The absorption maxima for dyes 2 and 3 including the electron-donating groups  $X = CH_3$  and  $X = OCH_3$  do not show significant changes according to that of dye 1. On the contrary, the absorption maxima move to longer wavelengths for dyes 4 and 5 including the electron-withdrawing groups X = CI and X = CN. A bathochromic shift results by increasing the intramolecular charge transfer from the indole ring to the azo unit with the electron-withdrawing groups at para position of the phenyl ring. However, this effect is more dominant for dye **5** than in dye **3** with the increase in the electron-withdrawing abilities of the substituent in all solvents. The obtained results are compatible with the experimental and theoretical data.

To further investigate the effects of the substituents and solvents for dyes **1–5**, the DFT calculations are carried out for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gaps. In calculations, the absorption maxima of dyes **1–5** were found to correspond to the electronic transitions from HOMO to LUMO. The obtained HOMO and LUMO orbitals for all dyes in gas phase are shown in Fig. 5. As can be seen in Fig. 5, for all dyes, each of the orbitals is delocalized over the whole of the main skeleton of the dye. In Table 5, HOMO, LUMO energies and energy gap ( $E_{gap}$ ) between the HOMO and LUMO for dyes **1–5** for the solvents are given. The obtained results



Fig. 3. a). A partial packing diagram for dye 2. (b). A view of the cyclic tetramer for dye 3 formed by C–H...O short contacts (shown as dashed lines). (c). A partial packing diagram for dye 4. (d). A packing diagram for dye 5 viewed down the *c*-axis.

indicate that, the energies of HOMO and LUMO are increased for dyes 2 and 3 as compared to dye 1. For dyes 2 and 3, the reason for increase in the energies of HOMO and LUMO is that the electron density on the whole system increases as a result of the electron-

#### Table 3

Tuble 5		
Parameters (Å,°) for hydrogei	n bonds and short intramolecular	contacts for dyes 2–5.

$X-H\cdots Cg(\pi-ring)$	H…Cg	X⋯Cg	$< Y - X \cdots Cg$	Symmetry codes
2				
C5-H5Cg3	2.90	3.587(4)	132	-x, ½+y, ½-z
C10–H10A…Cg2	2.66	3.525(4)	150	-x,-y,1-z,
C10–H10B…Cg1	2.75	3.488(4)	135	1-x,-y,1-z
3				
C17–H17F…Cg4	2.86	3.616(6)	137	1-x,-y,-z
C17–H17A…O1′	2.55	3.460(7)	158	2-x,2-y,2-z
C12'-H12'…O1	2.71	3.353(6)	127	x-1,+y,+z
4				
C5—H5…Cg3	2.91	3.598(6)	131	1-x,-1/2 + y,1/2-z
C10–H10A…Cg1	2.58	3.460(7)	153	-x,1-y,-z
C10–H10B…Cg2	2.78	3.523(7)	135	1-x,1-y,-z
5				
C9–H9B…Cg3	2.64	3.516(3)	152	-x,1-y,1-z
C10-H10A…Cg2	2.82	3.627(4)	143	1-x, 1-y,1-z.
$Cg(\pi\text{-ring})Cg(\pi\text{-ri})$	ng)	Cg	Cg	Symmetry codes
2				
Cg1 Cg1		3.627	7(2)	−x, − y, 1 − z
Cg3 Cg3		3.852	2(2)	1−x, −y, − z
3				
Cg1 Cg5 <sup>iii</sup>		3.732	2(2)	x—1, y, z
4				
Cg1 Cg1		3.665	5(6)	-x,1-y,-z
Cg3 Cg3		3.816	6(6)	-x,1-y,1-z
5				
Cg1 Cg1		3.626	6(6)	-x,1-y,-z

Cg1, Cg2, Cg3 and Cg4 are the centroids of the rings (N1/C1-C3/C8), (C3-C8), (C11-C16) and (C11'-C16'), respectively.

donating groups  $-CH_3$  and  $-OCH_3$  at para position of the phenyl ring. Contrary, the energies of HOMO and LUMO for dyes 4 and 5 decrease with respect to the corresponding values in dye 1, because of the decrease in the electron density with the effects of the electron-withdrawing groups. However,  $E_{gap}$  values for each dye decrease with the effects of both electron-donating and electronwithdrawing groups. At the same time, the solvent effects are little on the value of  $E_{gap}$ . When the dielectric constant ( $\varepsilon$ ) of the solvents increases, a small reducing in  $E_{gap}$  is seen in all dyes.

# 3.4. Molecular electrostatic potential (MEP)

The molecular electrostatic potential (MEP) is derived from the electronic density. MEP is a helpful tool to understand the sites of the electrophilic attack and the nucleophilic reactions as well as hydrogen-bonding interactions [35-37]. MEP at the B3LYP/6-311+G(d,p) optimized geometry was calculated to predict the reactive sites for the electrophilic and nucleophilic attacks in dyes **1–5**. The negative (red) and the positive (blue) regions of the MEP were related to the electrophilic and nucleophilic reactivities, respectively, as shown in Fig. 6. As can be seen in Fig. 6, the

Table	4
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Calculated and experimental absorption wavelengths ( $\lambda_{max}$ ) for dyes **1–5** in different solvents. The oscillator strengths (*f*) are given in parentheses.

Dve	DMSO		A Acid		Chloroform		
Dyc	DIVISO	DIVISO					
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
1	387	390 (0.94)	385,437	387 (0.92)	380	388 (0.94)	
2	387	393 (1.01)	385,448	389 (1.00)	382	390 (1.01)	
3	389	399 (1.07)	384,466	396 (1.05)	384	397 (1.07)	
4	393	398 (1.03)	387	395 (1.02)	386	396 (1.03)	
5	414	420 (1.14)	407	416 (1.11)	406	418 (1.13)	



Fig. 4. Protonated azo form and its resonance stabilized iminium-hydrazone structure.

negative regions are mainly localized on the diazo groups in the dyes. Additionally, the negative potential sites are the oxygen atom in dye **3** and the nitrogen atom of the cyano group in dye **5**. The positive potential sites are the hydrogen atoms of methyl groups on indole ring and around the hydrogen atoms of the methoxy groups in dye **3**.

# 3.5. Dipol moments

Table 5 also shows a comparison of the dipole moments of dyes **1–5** in different solvents. While the dipole moments of dyes **2** and **3** decrease with the electron-donating groups, the dipole moments of dyes **4** and **5** increase with the electron-withdrawing groups with



Fig. 5. Computed orbitals for dyes (1–5).

Table 5HOMO-LUMO orbital energies,  $E_{gap}$  and dipole moment values for dye 1–5 in different solvents.

Dye	μ (Debye)	HOMO (eV)	LUMO (eV)	$E_{\rm gap}({\rm eV})$	μ (Debye)	HOMO (eV)	LUMO (eV)	$E_{\rm gap}({\rm eV})$	μ (Debye)	HOMO (eV)	LUMO (eV)	$E_{\rm gap}~({\rm eV})$
	DMSO				Acetic acid				Chloroform			
1	6.53	-5.73	-2.23	3.50	5.960	-5.67	-2.16	3.51	5.782	-5.65	-2.13	3.52
2	5.76	-5.65	-2.17	3.48	5.247	-5.59	-2.09	3.50	5.086	-5.57	-2.06	3.51
3	3.87	-5.52	-2.09	3.43	3.452	-5.46	-2.01	3.45	3.325	-5.45	-1.98	3.47
4	8.78	-5.75	-2.32	3.43	8.143	-5.71	-2.27	3.44	7.941	-5.70	-2.25	3.45
5	13.80	-5.89	-2.66	3.23	12.952	-5.88	-2.62	3.26	12.673	-5.88	-2.61	3.27

respect to that of dye **1** in each solvent. Similarly, the solvent effects on the dipole moments of dyes **1–5** are not pronounced.

# 4. Conclusions

In summary, a new series of phenylazoindole based dyes were synthesized and fully characterized. The molecular structures of the dyes were characterized by using X-ray structural analyses and compared with the theoretical calculations. Generally, the obtained experimental data are compared with the theoretical calculations and the results are compatible but all of the computed N<sub>2</sub>=N<sub>3</sub> bonds are slightly shorter than the experimental ones. The molecular structures of the dyes are stable in different solvent media. The dyes have strong single absorption bands in all solvents except of acetic acid. In acetic acid, the dyes (**1**–**3**) were protonated via  $\beta$ -nitrogen atom of the azo group.



**Fig. 6.** MEP map calculated at B3LYP/6-311+(d,p) level for (a) dye **1**, (b) dye **2**, (c) dye **3**, (d) dye **4**, (e) dye **5**.

(e)

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#### Appendix A. Supplementary material

**CCDC**-924115, 924116, 937360 and 924117 contain the supplementary crystallographic data for the structures **2–5** respectively. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ ccdc.cam.ac.uk).

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