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Synthesis, solvatochromic properties and theoretical calculation of some novel disazo indole dyes



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A R T I C L E I N F O

ABSTRACT

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1. Introduction

Azo dyes are organic compounds consisting of a diazotized amine coupled to a coupling component and contain one or more azo (-N=N-) linkages. In recent years, because of their properties, considerable attention has been drawn toward the synthesis of azo dyes. Azo dyes are the largest class of industrial synthesized organic dyes due to their applications, such as dye sensitized solar cells [1], non-linear optical systems [2], metallochromic indicators [3], sensors [4], photochromic materials [5], photo-sensitizers [6], biological-medical studies [7] and computational studies [8]. Explorations of disazo dyes having aromatic heterocycles are very significant because they have shown brilliant color, excellent light, good tinctorial strength and washing fastness. Pyrazole and indole dyes have been shown to be important colorants for yellow to orange dyes in industrial applications. Also, due to their piquant electronic and geometrical features, theoretical calculations of heterocyclic compounds have been trend by several research groups [9,10]. The biological importance of indole and its pharmacological and medical potential have made indole extremely fascinating and rewarding research targets and have motivated researchers to study its synthesis and investigation on its properties [11,12].

In the literature, one study was found on synthesis of indole disazo dyes [13]. In that study, 4,4'-diaminodiphenylsulfonamide (DADPSA) and 4,4'-diaminodiphenylurea (DADPU) are used as carbocyclic diazo

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Synthesis of new disazo indole dyes (**3a–3m**) was carried out by diazotization of 5-amino-4-arylazo-3-methyl-1H-pyrazoles (**2a–2m**) and coupling with 2-phenyl indole. The newly synthesized 12 disperse disazo dyes were characterized by UV–vis, FT-IR, ¹H NMR and elemental analysis. Their solvatochromic properties in different solvents were investigated. In addition, theoretical calculations are performed for the disazo dyes. The molecular structures of all synthesized dyes **3a–3m** have been optimized to the global minima at the levels of using HF and DFT methods with 6-311G(d), 6-311G(d), 6-311+G(d,p), and 6-31++G(d,p) basis sets.

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component. Heterocyclic compounds are used as both diazo component and coupling component.

It is very important to synthesize and characterize new disazo dyes experimentally to provide guidance for further studies. So, in this study, synthesis of new disazo indole dyes (**3a–3m**) was carried out by diazotization of 5-amino-4-arylazo-3-methyl-1H-pyrazoles (**2a–2m**) and coupling with 2-phenyl indole. All synthesized disperse disazo dyes were characterized by UV–vis, FT-IR, ¹H NMR and elemental analysis. Their solvatochromic properties in different solvents were investigated. Also, the vibrational frequencies and optimized structure parameters of heterocyclic disazo dye (**3a–3m**) have been calculated by using HF and DFT methods at 6-31G(d,p) basis set level. All computations have been performed using Gaussian 09.A1 package and GaussView 5.0.8 molecular visualization program on personal computer. All spectroscopic properties examined with the experimental techniques were supported with the computed results.

2. Experimental

2.1. Material and methods

Chemicals used for the synthesis of the compounds were obtained from Aldrich and Merck Chemical Company without further purification. The solvents used were of spectroscopic grade.

IR spectra were determined using a Schimadzu IR Prestige-21 Fourier Transform-infrared (FT-IR) spectrophotometer on a KBr disc. Nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker Ultrashield Superconducting 400 MHz NMR in deuterated



Fig. 1. Synthesis of 2-arylhydrazono-3-ketiminobutyronitriles (1a-1m) and 5-amino-4-arylazo-3-methyl-1H-pyrazoles (2a-2m).



Fig. 2. Synthesis of 2-phenyl-3-(3-methyl-4-arylazo-5-diazenyl-1H-pyrazole)-1H-indole (3a-3m).

dimethylsulfoxide (DMSO-d₆) using tetramethylsilane (TMS) as the internal reference; chemical shifts were (δ) given in ppm. Ultravioletvisible (UV-vis) absorption spectra were recorded on a Schimadzu UV-1601 double beam spectrophotometer at the wavelength of maximum absorption (λ_{max}) in a range of solvents, i.e. DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform at the various concentrations $(1 \times 10^{-6} - 1 \times 10^{-8})$. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected. Elemental analysis was done on a Leco CHNS-932 analyzer. LC-ESI-MS analyses were recorded on Agilent 1100 MSD.

Table 1Elemental analysis of dyes 3a-3m.

Dye	Х	m.p. (°C)	Yield (%)	Color	Molecular formula (m. wt)	Elemental analysis	: calc. (found)	
						%C	%Н	%N
3a	0-NO2	237–238	75	Dark red	$C_{24}H_{18}N_8O_2$ (450.45)	63.99 (63.92)	4.03 (4.10)	24.88 (24.68)
3b	m-NO ₂	304–305	72	Dark red	C ₂₄ H ₁₈ N ₈ O ₂ (450.45)	63.99 (63.94)	4.03 (4.02)	24.88 (24.68)
3c	p-NO ₂	255-256	76	Dark red	C ₂₄ H ₁₈ N ₈ O ₂ (450.45)	63.99 (63.94)	4.03 (4.10)	24.88 (24.68)
3d	o-CH ₃	250–251	68	Light red	C ₂₅ H ₂₁ N ₇ (419.48)	71.58 (71.60)	5.05 (5.08)	23.37 (23.32)
3e	m-CH ₃	203–204	69	Dark red	C ₂₅ H ₂₁ N ₇ (419.48)	71.58 (71.61)	5.05 (5.06)	23.37 (23.33)
3f	p-CH ₃	237–238	65	Red	C ₂₅ H ₂₁ N ₇ (419.48)	71.58 (71.56)	5.05 (5.07)	23.37 (23.37)
3h	<i>m</i> -OCH ₃	210-211	63	Dark red	C ₂₅ H ₂₁ N ₇ O (435.48)	68.95 (68.98)	4.86 (4.84)	22.51 (22.53)
3i	p-OCH ₃	244-245	68	Red	C ₂₅ H ₂₁ N ₇ O (435.48)	68.95 (68.96)	4.86 (4.88)	22.51 (22.49)
3j	o-Cl	261–262	70	Red	C ₂₄ H ₁₈ N ₇ Cl (439.90)	65.53 (65.55)	4.12 (4.10)	22.29 (22.32)
3k	m-Cl	100–101 (decomposition)	73	Light red	C ₂₄ H ₁₈ N ₇ Cl (439.90)	65.53 (65.50)	4.12 (4.14)	22.29 (22.27)
31	p-Cl	234-235	71	Red	C ₂₄ H ₁₈ N ₇ Cl (439.90)	65.53 (65.51)	4.12 (4.11)	22.29 (22.30)
3m	Н	197–198	68	Dark red	$C_{24}H_{19}N_7$ (405.45)	71.09 (71.10)	4.72 (4.73)	24.18 (24.16)



Fig. 3. Tautomeric structures of 3a-3m.

2.2. Synthesis of azo dyes

2.2.1. Synthesis of 2-arylhydrazono-3-ketiminobutyronitriles (1a-1m) and 5-amino-4-arylazo-3-methyl-1H-pyrazoles (2a-2m)

2-Arylhydrazono-3-ketiminobutyronitriles (1a-1m) and 5-amino-4-arylazo-3-methyl-1H-pyrazoles (2a-2m) were prepared according to the literature procedures [14,15]. The general route for the synthesis

of 2-arylhydrazono-3-ketiminobutyronitriles and 5-amino-4-arylazo-3-methyl-1H-pyrazoles is shown in Fig. 1.

2.2.2. Synthesis of 2-phenyl-3-(3-methyl-4-arylazo-5-diazenyl-1Hpyrazole)-1H-indole (**3a-3m**)

5-Amino-4-arylazo-3-methyl-1H-pyrazoles (2a-2m) (0.63 g, 3.0 mmol) were dissolved in hot glacial acetic acid/propionic acid

Table 2			
Spectral data	ı for	dyes	3a-3m.

	FT-IR (cm ⁻	¹ , KBr)		¹ H NMR (d, ppm, in DMS	D-d ₆)	
	v_{Ar-H}	v_{Alip-H}	$\nu_{N=N}$	AroH	AlipH	Х-Н
3a	3350	2958	1525	8.52-7.30 (m, 13H)	2.41 (s, 3H, pyrazole CH ₃)	12.59 (indole or T ₁) (br)
						13.56 (pyrazole or T ₂) (br)
3b	3172	2966	1533	8.66–7.33 (m, 13H)	2.56, (s, 3H, pyrazole CH_3)	12.58 (indole or T_1) (br)
						13.53 (pyrazole or T ₂) (br)
3c	3186	2920	1520	8.65–7.19 (m, 13H)	2.56 (s, 3H, pyrazole CH ₃)	12.49–12.75 (indole or T ₁)
						13.59 (pyrazole or T_2) (br)
3d	3080	2890	1550	8.96–7.21 (m, 13H)	1.3 (s, 3H, toluidine CH_3)	8,40 (indole or T_1) (br)
					2.63 (s, 3H, pyrazole CH ₃)	8,80 (pyrazole or T ₂) (br)
3e	3320	2975	1540	8.68-6.92 (m, 13H)	2.16–2.20 (s, 3H, toluidine CH ₃)	8.50 (indole or T ₁) (br)
					2.37–2.40 (s, 3H, pyrazole CH ₃)	11.50 (pyrazole or T_2) (br)
3f	3240	2925	1530	8.90-7.11 (m, 13H)	1.18–1.19 (s, 3H, toluidine CH ₃)	8.10 (indole or T ₁) (br)
					2.40–2.60 (s, 3H, pyrazole CH ₃)	8.72 (pyrazole or T ₂) (br)
3h	3320	2820	1540	8.25-6.95 (m, 13H)	2.56 (s, 3H, pyrazole CH ₃)	8.70 (indole or T ₁) (br)
					3.85 (s, 3H, anisidine OCH ₃)	8.98 (pyrazole or T ₂) (br)
3i	3110	2886	1540	8.10-6.89 (m, 13H)	2.65–2.67 (s, 3H, pyrazole CH ₃)	8.40 (indole or T ₁) (br)
					3.94 (s, 3H, anisidine OCH ₃)	8.80 (pyrazole or T ₂) (br)
3j	3040	2968	1570	8.18-7.08 (m, 13H)	2.70 (s, 3H, pyrazole CH_3)	8.05 (indole or T_1) (br)
-						8.85 (pyrazole or T_2) (br)
3k	3320	2947	1540	8.20-6.97 (m, 13H)	2.60 (s, 3H, pyrazole CH_3)	8.70 (indole or T_1) (br)
						10.65 (pyrazole or T_2) (br)
31	3310	2892	1550	8.22-7.18 (m, 13H)	2.55 (s, 3H, pyrazole CH_3)	8.68 (indole or T ₁) (br)
						9.8 (pyrazole or T_2) (br)
3m	3200	2920	1535	8.6-7.10 (m. 14H)	2.5 (s. 3H, pyrazole CH_3)	8.20 (indole or T_1) (br)
					(,, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	8.96 (pyrazole or T_2) (br)
						······································

T₁: hydrazo form of indole.

T₂: hydrazo form of pyrazole.

mixture (2:1, 9.0 ml) and were speedily cooled in an ice–salt bath to -5 °C. The mixture was then stirred for 4 h at 0–5 °C. The solution was then added in pieces during 1 h to a cold solution of nitrosyl sulfuric acid [prepared from sodium nitrite (0.22 g) and concentrated sulfuric acid (4.5 ml)]. The mixture was stirred 4 h at 0 °C after addition. The progress of the reaction was followed with pH meter. Excess nitrous acid was removed by the addition of urea. The resulting diazonium salt was added to cold solution of 2-phenylindole (0.58 g, 3.0 mmol) dissolved in a mixture of acetic acid/propionic acid (3:1, 12 ml). During the addition of diazonium salt, the reaction mixture was stirred and pH was maintained at 4–6 by addition of saturated sodium carbonate solution. The mixture was stirred for a further 24 h at 5 °C. The resulting product was filtered, washed with water several times, dried in a

vacuum oven at 50 °C and crystallized from DMF-H₂O. The general route for the synthesis of 2-phenyl-3-(3-methyl-4-arylazo-5-diazenyl-1H-pyrazole)-1H-indole (**3a-3m**) is shown in Fig. 2.

2.3. Theoretical calculations

Gaussian approximates orbital shapes and orbital energies of a given molecular geometry using a model chemistry consisting of two parts: a basis set and a method. Calculations using large basis sets are more accurate because they are less restrictive on the location of the electrons. Such calculations are also more expensive because they require computing more integrals. DFT methods account for electron correlation by estimating the interaction of an electron with the total electron



Fig. 4. ¹H NMR spectra of dyes 3a and 3b.

Table 3

Theoretical NMR calculations for dyes **3a–3m**.

	6-31G(d)			6-311G(d)			6-311++0	G(d,p)		6-31++G	(d,p)	
	AroH	AlipH	Х-Н	Aro.–H	Alip.–H	Х–Н	AroH	Alip.–H	X-H	Aro.–H	AlipH	Х–Н
3a	8.75-7.21	2.47-2.21	7.64	9.02-7.48	2.70-2.49	7.98 (indole or T ₁)	9.13-7.64	2.62-2.50	8.39	9.29-7.65	2.68-2.44	8.50
	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole CH ₃)	9.24 (pyrazole or T ₂)	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T_1)
			$(\text{pyrazole or } T_2)$						9.08 (pyrazole or T_2)			$(\text{pyrazole or } T_2)$
3b	9.05-7.24	2.47-2.23	7.60	9.35-7.51	2.71-2.69	7.93 (indole or T ₁)	9.52-7.70	2.76-2.73	8.46	9.67-7.71	2.73-2.42	8.68
	(m,13H)	(s, 3H, pyrazole CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole CH ₃)	9.34 (pyrazole or T ₂)	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T ₁)	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T ₁)
			9.11 (p_{T})						9.84			10.00
3c	8.78-7.24	2.48-2.22	(pyrazoic or 12) 7.67	9.05-7.50	2.73-2.50	8.01 (indole or T_1)	9.29-7.62	2.78-2.54	(pyrazoic or 12) 8.44	9.27-7.66	2.76-2.43	(pyrazoic or 12) 8.57
	(m,13H)	(s, 3H, pyrazole CH ₃)	(indole or T ₁)	(m, 13H)	(s, 3H, pyrazole CH ₃)	9.35 (pyrazole or T ₂)	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T ₁)	(m, 13H)	(s, 3H, pyrazole CH ₃)	(indole or T ₁)
			9.11						9.85			10.03
34	8 65-7 23	2 48_2 17	(pyrazole or T ₂) 7 56	8 92_7 52	2 75_2 47	7.90 (indole or T _c)	9 17_7 66	2 78_2 49	(pyrazole or T ₂) 8 37	9 12_7 70	2 73_2 40	(pyrazole or T ₂) 8 39
Ju	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	9.32 (pyrazole or T_2)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T ₁)
		3.05-2.27	9.08		3.28-2.54	(1) 2)		3.44-2.61	9.70		3.25-2.52	9.90
		(s, 3H, toluidine, CH ₃)	(pyrazole or T ₂)		(s, 3H, toluidine, CH ₃)	=		(s, 3H, toluidine, CH ₃)	(pyrazole or T ₂)		(s, 3H, toluidine, CH ₃)	(pyrazole or T ₂)
3e	8.84 - 7.23	2.46-2.16	7.57 (indolo or T.)	9.11 - 7.51	2.72 - 2.46	7.92 (indole or T_1)	9.33 - 7.63	2.78-2.48	8.35 (indole or T.)	9.32 - 7.64	2.74–2.38 (s. 2H. purazolo, CH.)	8.43 (indolo or T.)
	(111, 1311)	(s, 511, pyrazole, C113) 2.63–2.12	9.06	(111, 1311)	(s, 511, pyrazole, C113) 2.81–2.40	9.50 (pyrazore or 12)	(111, 1511)	(s, 511, pyrazole, C113) 2.80–2.29	9.75	(111, 1511)	(s, 511, pyrazole, C113) 2.70–2.24	9.91
		(s, 3H, toluidine, CH ₃)	(pyrazole or T ₂)		(s, 3H, toluidine, CH ₃)			(s, 3H, toluidine, CH ₃)	(pyrazole or T ₂)		(s, 3H, toluidine, CH ₃)	(pyrazole or T ₂)
3f	8.82-7.23	2.45-2.16	7.57	9.09-7.51	2.72-2.45	7.91 (indole or T ₁)	9.56-7.88	3.00-2.72	8.58	9.30-7.65	2.66-2.37	8.43
	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	$(s, 3H, pyrazole, CH_3)$	9.29 (pyrazole or T ₂)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)
		(s. 3H. toluidine, CH ₃)	(pyrazole or T ₂)		(s, 3H, toluidine, CH ₃)			(s. 3H. toluidine, CH ₃)	(pyrazole or T ₂)		(s. 3H. toluidine. CH ₃)	(pyrazole or T ₂)
3h	8.85-6.71	2.45-2.16	7.56	9.14-6.89	2.71-2.46	7.90 (indole or T1)	9.36-7.08	2.74-2.48	8.35	9.34-7.16	2.73–2.38	8.48
	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	9.31 (pyrazole or T ₂)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)
		4.09-3.73 (s 3H anisidine (Ha)	9.07 (pyrazole or T _e)		4.25-3.82 (s 3H anisidine (Ha)			4.29-3.85 (s 3H anisidine CHa)	9.81 (pyrazole or T _a)		4.28–3.84 (s_3H_anisidine_CHa)	10.01 (pyrazole or T _e)
3i	8.81-6.81	2.45–2.15	(pyruzoie or 1 ₂) 7.54	9.09-6.95	2.72–2.44	7.88 (indole or T_1)	9.32-7.03	2.75–2.46	(pyrazore or 1 ₂) 8.32	9.28-7.08	2.72–2.36	(pyruzoic or 1 ₂) 8.44
	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T ₁)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	9.26 (pyrazole or T ₂)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T ₁)
		4.07–3.77	9.03		4.23–3.85			4.28–3.89	9.73		4.32–3.93	9.93
3i	8 91-7 21	(S, 3H, anisidine, CH ₃) 2 42–2 17	(pyrazole or 1 ₂) 7 58	9 19-7 50	(s, 3H, anisidine, CH ₃) 2 67–2 46	7.93 (indole or T_1)	9 58-7 88	(s, 3H, anisidine, CH ₃) 2 99–2 75	(pyrazole or 1 ₂) 8 59	9 34-7 63	(s, 3H, anisidine, CH ₃) 2 73–2 41	(pyrazole or 1 ₂) 8 44
5)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T ₁)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	9.32 (pyrazole or T_2)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T ₁)	(m, 13H)	(s, 3H, pyrazole, CH ₃)	(indole or T ₁)
			9.08						9.95			9.90
21,	0 01 7 17	2 42 2 17	(pyrazole or T ₂)	0.00 7.20	269 246	705 (indolo or T)	0.20 7.60	272 247	(pyrazole or T ₂)	0.20 7.62	270 229	(pyrazole or T ₂)
эк	o.o1-7.17 (m. 13H)	$(s, 3H, pyrazole, CH_2)$	(indole or T_1)	(m. 13H)	$(s, 3H, pyrazole, CH_2)$	9.31 (pyrazole or T_2)	9.29-7.60 (m. 13H)	$(s, 3H, pyrazole, CH_2)$	(indole or T_1)	9.28-7.82 (m. 13H)	$(s, 3H, pyrazole, CH_2)$	(indole or T_1)
	(,)	(-,, F J, <u>3</u>)	9.08	(,)	(-,, F J, <u>3</u>)	(FJ	(,)	(-,, բ.),3/	9.79	(,)	(-,, FJ , <u>3</u>)	9.97
			(pyrazole or T ₂)						(pyrazole or T ₂)			(pyrazole or T ₂)
31	8.77 - 7.22	2.44-2.17	7.60 (indolo or T)	9.04 - 7.49	2.69–2.46	7.94 (indole or T_1)	9.28 - 7.62	2.76-2.50	8.37 (indolo or T)	9.26 - 7.64	2.72–2.39	(indolo or T)
	(111, 150)	(S, SH, Pyrazole, CH ₃)	(Indole of 1 ₁) 9.06	(111, 150)	$(S, SH, PYIAZOIE, CH_3)$	9.50 (pyrazole of I_2)	(111, 150)	(S, SH, Pyrazole, CH ₃)	(Indole of 1 ₁) 9.80	(111, 150)	$(S, SH, PYIAZOIE, CH_3)$	(Indole of 1 ₁) 9.97
			(pyrazole or T ₂)						(pyrazole or T ₂)			(pyrazole or T ₂)
3m	8.84-7.23	2.47-2.18	7.57 (indole or T_1)	9.41-7.80	3.02-2.76	8.19 (indole or T_1)	9.38-7.65	2.80-2.50	8.33	9.34-7.69	2.76-2.42	8.40
	(m, 14H)	(s, 3H, pyrazole, CH ₃)	9.07	(m, 14H)	(s, 3H, pyrazole, CH ₃)	9.60 (pyrazole or T ₂)	(m, 14H)	(s, 3H, pyrazole, CH ₃)	(indole or T_1)	(m, 14H)	(s, 3H, pyrazole, CH ₃)	$($ indole or $T_1)$
			(Pyrazoic or 12)						(pyrazole or T ₂)			(pyrazole or T ₂)

T₁: hydrazo form of indole. T₂: hydrazo form of pyrazole.

Table 4

Sum of electronic and zero-point energies (Hartree/particle) of dyes **3a-3m** at DFT (B3LYP).

Dye no.	6-31G(d)	Dipole moment (Debye)	6-311G(d)	Dipole moment (Debye)	6-311++G(d,p)	Dipole moment (Debye)	6-31++G(d,p)	Dipole moment (Debye)
3a 3b 3c 3d 3e 3f 3h 3i 2:	- 1513,280578 - 1513,293310 - 1513,29353 - 1348,078702 - 1348,083552 - 1348,083983 - 1423,282351 - 1423,284339 1708 280521	4,200 5,906 11,332 6,046 6,045 5,674 5,459 3,939 5,320	- 1513,616506 - 1513,628682 - 1513,628464 - 1348,364632 - 1348,369924 - 1348,370235 - 1423,590004 - 1423,591897 1269,624677	4,322 5,903 11,336 6,158 6,139 5,743 5,530 3,956 5,502	- 1513, 676437 - 1513,688262 - 1513,688552 - 1348,421208 - 1348,426638 - 1348,427021 - 1423,649863 - 1423,651718 1778,740942	4,757 6,022 11,510 6,039 6,030 5,539 5,372 3,806 5,415	- 1513, 369284 - 1513, 354855 - 1513, 382283 - 1348, 162283 - 1348, 167629 - 1348, 168033 - 1423, 369968 - 1423, 371798	4,841 5,832 11,662 6,088 6,073 5,601 5,439 3,862 5,437
3j 3k 31 3m	- 1768,388631 - 1768,399185 - 1768,399362 - 1308,793093	5,329 5,938 7,547 6,034	- 1768,694677 - 1768,705404 - 1768,705552 - 1309,071896	5,503 6,034 7,684 6,125	- 1768,748943 - 1768,759108 - 1768,759127 - 1309,126231	5,415 5,794 7,306 5,973		5,437 5,852 7,384 6,029



Fig. 5. The calculated optimized structures of dyes 3a-3m.



Fig. 5 (continued).

density. DFT orbitals are formed from basic functions like those used in SCF or MP2. Most popular DFT method is B3LYP (Becke3-Parameter method for calculating that part of the molecular energy due to overlapping orbitals, plus the Lee–Yang–Parr method of accounting for correlation) [16].

All the calculations were performed by using Gaussian 09.A1 program on a personal computer and GaussView 5.0.8 was used for visualization of the structure and simulated vibrational spectra [17]. The molecular structures of all disazo dyes **3a–3m** have been optimized to the global minima at the levels of using HF and DFT methods with 6-31G(d), 6-311G(d), 6-311++G(d,p) and 6-31++G(d,p) basis sets. Time-dependent DFT (TDDFT) calculations were then performed with the same functional and basis set at the optimized geometry to obtain electronic transition energies. Oscillator strengths were deduced from the dipole transition matrix elements (for singlet states only).

3. Results and discussion

The selected physical properties of the synthesized dyes **3a–3m** were measured and listed in Table 1.

Tautomerism is significant for areas of chemistry. Especially, the azohydrazone tautomerism is interesting for theoretical studies. Tautomers have different properties. Azo dyes are mostly in hydrazone form. Disazo dyes **3a–3m** can exist in four possible tautomeric forms, namely the disazo-enamine form, the hydrazo-azo-enamine form, the azohydrazo-imine and the dishydrazo-imine form as shown in Fig. 3. ¹H NMR spectra and FT-IR spectra of dyes are presented in Table 2. ¹H NMR spectra of dyes **3a–3m** showed broad peaks at 12.75–8.05 ppm (NH) of indole or hydrazo form of indole and 13.59-8.72 ppm (NH) of pyrazole or hydrazo form of pyrazole, respectively. The other δ values of 2.70–2.37 ppm (CH₃) and 8.96–6.92 ppm (aromatic H) were recorded. **3d–3f** showed broad peaks at 2.20–1.18 ppm (CH₃) of toluidine. **3h** and **3i** showed broad peaks at 3.94–3.85 ppm (OCH₃) of anisidine. ¹H NMR spectra of dyes **3a** and **3b** are illustrated in Fig. 4. ¹H NMR chemical shift values have been obtained by using the gauge including atomic orbital (GIAO)-DFT method at the same functional and basis set and listed in Table 3. Comparing experimental data with theoretical NMR chemical shifts provides practical information on the chemical structures of compounds. The FT-IR spectra of dyes 3a-3m showed imino (NH) band at 3350–3040 cm⁻¹, aromatic (Ar–H) band at 2975–2886 cm⁻¹ and azo (N=N) band at 1570–1520 cm⁻¹ were recorded. There is a generally excellent agreement between the theoretical and experimental data, with the differences in only a few wavenumbers. These suggest that these disazo dyes are predominantly in one of the hydrazo-azo-enamine or the azo-hydrazo-imine forms as opposed to the disazo-enamine and dishydrazo-imine forms, in the solid state.

Calculated energies and energy difference for all basis sets of **3a–3m** were determined by B3LYP and different basis sets were presented in Table 4. The basis set size effect on the calculated energies. There is a little difference between basis sets. Using the basis sets of larger sizes gives rise to increases in the differences between the calculated energies of **3a–3m**.

The optimized structures of **3a–3m** were shown in Fig. 5 with numbering of the atoms. The vibrational frequencies and optimized structure parameters of disazo dye 3a have been calculated by using DFT methods at 6-31G(d), 6-311G(d), 6-311++G(d,p), and 6-31++G(d,p) basis set level and listed in Table 5.

Table 5

Calculated vibrational frequencies, bond length and bond angle of dye 3a.

UV spectrum analyses of **3a-3m** have been investigated experimentally and theoretically. Absorption spectra of dyes **3a** and **3b** are illustrated in Fig. 6. The UV spectrum of compounds was measured in six different solvents acetonitrile, acetic acid, methanol, chloroform, DMF and DMSO. The absorption maxima of the compounds have been found by using Self-Consistent Field (SCF) method at 6-31G(d), 6-311G(d), 6-311++G(d,p), and 6-31++G(d,p) level and listed in Table 6. The UV-vis absorption spectra of dyes **3a-3m** were recorded in the range of λ between 350 and 600 nm, using a variety of solvents in concentrations $(1 \times 10^{-6} - 1 \times 10^{-8} \text{ M})$. The visible absorption spectra of the dyes did not correlate with the polarity of solvent. Single maximum is seen in the spectra of the compound **3a-3m** in all used solvents. When compared with λ_{max} values of obtained disazo dyes, λ_{max} of dyes in DMF showed more bathochromic shifts than λ_{max} of dyes in the other solvents except for **3a**, **h** and **l**. λ_{max} of **3c** does not significantly change in all used solvents. Hypsochromic shift is seen in the spectra of compound **3d** in methanol. The obtained disazo dyes gave a single dominant absorption peak without a shoulder in all used solvents. It can be said that the maximum values in all solvents are very close to each other and don't change much.

Theoretically computed thermo dynamical parameters such as the SCF energy, zero-point vibrational energies (ZPVE), the entropy, the heat capacity, rotational constants and dipole moment have been presented in Table 7. Based on the vibrational analysis at B3LYP/6-311++G(d,p) level, the standard statistical thermodynamic functions: heat capacity, entropy and enthalpy changes for the compound studied were obtained from the theoretical harmonic frequencies.

4. Conclusions

In this work, we performed the experimental and theoretical vibrational analysis of **3a–3m**. A series of twelve novel containing indole

Parameters (stretching)	Calculated frequencie (cm ⁻¹)	l es	Calculated bor 6-31G(d,p)	nd length	Parameters (bending)	Calculated frequencie (cm ⁻¹)	l es	Calculated I 6-31G(d,p)	oond angle
	DFT	HF	DFT	HF		DFT	HF	DFT	HF
N(6)-H(4)	3662	3915	1.007670	0.991870	C(3)-N(5)-N(6)	794	1567	106.11	106.75
N(18)-H(49)	3647	3898	1.007799	0.992305	C(38)-C(40)-C(44)	632	674	120.14	120.07
C(20)-H(24)	3238	3403	1.079912	1.070810	C(15)-C(20)-C(23)	1109	946	118.40	118.46
C(7)-H(8)	3122	3269	1.091034	1.082589	C(2)-N(11)-N(12)	948	29	112.55	112.89
N(12)-C(16)	1414	1504	1.363628	1.377267	C(2)-C(1)-N(14)	593	410	122.01	122.55
C(39)-H(43)	3213	3368	1.081375	1.073132	N(50)-C(29)-C(28)	1497	374	115.79	115.90
C(7)-H(9)	3094	3246	1.092540	1.083787	H(49)-N(18)-C(48)	1240	1644	124.84	125.17
C(7)-H(8)	3040	3187	1.091034	1.082589	H(22)-C(19)-C(48)	1174	1391	121.62	121.49
C(19)-H(22)	3167	3320	1.084365	1.075678	H(8)-C(7)-H(9)	1431	1596	109.54	109.49
C(27)-H(33)	3190	3352	1.083240	1.074222	C(19)-C(21)-C(23)	593	946	121.10	121.12
C(38)-H(41)	3163	3322	1.084669	1.075538	C(31)-C(30)-N(13)	496	639	116.03	116.04
C(42)-H(46)	3181	3341	1.084141	1.075243	H(9)-C(7)-H(10)	1474	1602	106.59	107.38
C(27)-C(32)	1058	1129	1.394474	1.384293	H(8)-C(7)-H(10)	1431	1567	109.44	109.38
N(5)-C(3)	1414	1380	1.324513	1.296099	N(6)-C(2)-N(11)	148	29	126.15	125.45
C(1)-C(2)	1085	1777	1.409257	1.375574	H(26)-C(23)-C(20)	1174	1391	118.96	119.21
N(50)-C(29)	380	1209	1.478871	1.467019	H(33)-C(27)-C(28)	1338	1596	119.73	119.81
N(11)-N(12)	1431	1803	1.279077	1.226644	H(34)-C(28)-C(29)	1497	1657	119.06	119.29
C(15)-C(20)	1618	1793	1.401708	1.397484	H(41)-C(38)-C(40)	1639	1793	119.37	119.57
C(19)-C(48)	1653	1803	1.391983	1.388772	H(45)-C(40)-C(44)	1185	1793	120.16	120.20
C(19)-C(21)	1304	1793	1.391280	1.377582	O(51)-N(50)-C(29)	593	959	117.64	117.65
C(27)-C(28)	1610	1777	1.391799	1.382879	C(1)-N(14)-N(13)	148	639	116.22	116.67
C(31)-C(32)	1474	1315	1.389268	1.382818	O(52)-N(50)-O(51)	862	759	125.29	125.31
C(38)-C(40)	1014	1793	1.391086	1.384320	C(17)-C(16)-N(12)	150	696	120.96	121.03
C(39)-C(42)	1639	1594	1.390852	1.383770	C(17)-C(37)-C(39)	380	363	121.17	121.02
C(37)-C(39)	1304	1758	1.404862	1.391699	C(20)-C(23)-C(21)	573	639	121.51	121.31
N(6)-C(2)	1085	1425	1.350210	1.329226	C(21)-C(19)-C(48)	884	616	117.07	117.18
C(20)-C(23)	1520	1639	1.390639	1.377867	C(29)-C(28)-C(27)	585	616	119.81	119.62
C(21)-C(23)	1035	1765	1.404318	1.400217	C(27)-C(32)-C(31)	916	759	120.12	120.24
C(16)-C(17)	1561	1437	1.407623	1.371410	C(28)-C(27)-C(32)	803	1017	119.67	119.55
C(40)-C(44)	1613	1199	1.394034	1.384910	C(7)-C(3)-N(5)	585	592	120.39	120.69
N(14)-C(1)	1316	759	1.372540	1.385201					



Fig. 6. Absorption spectra of dyes 3a and 3b.

cycle disperse azo dyes **3a–3m** were synthesized in reasonably good yields. The newly synthesized compounds were characterized by ¹H NMR, mass spectrometry, IR studies and elemental analysis. Also, absorption ability of these compounds, solvent influence on the wavelength of maximum absorption, was studied. The visible absorption spectra of the dyes did not correlate with the polarity of solvent. In addition, theoretical studies of novel disazo dyes were evaluated. The vibrational frequencies, optimized molecular structures and corresponding vibrational assignments of heterocyclic disazo dyes (**3a–3m**) have been

calculated using HF and DFT (B3LYP) methods at 6-31G(d), 6-311G(d), 6-311++G(d,p) and 6-31++G(d,p) basis set level. The calculated wavenumbers were compared with experimental FT-IR. We performed ¹H chemical shifts of **3a–3m**. The positions of hydrogen atoms of molecules were determined by means of computed ¹H chemical shifts. Also, UV spectrum analyses of **3a–3m** have been investigated theoretically. The data were compared with the experimental results. There is generally an excellent agreement between the theoretical and experimental data, with the differences in only a few values.

Table 6 Influence of solvent on λ_{max} (nm) of dyes 3a–3m.

	Experimental						B3LYP/6-311+	++g(d,p)				
	Acetonitrile	Acetic acid	Methanol	Chloroform	DMF	DMSO	Acetonitrile	Acetic acid	Methanol	Chloroform	DMF	DMSO
3a	486	466	475	486	485	485	515	512	522	513	517	517
3b	485	485	478	485	486	476	495	496	497	500	498	497
3c	486	485	486	486	486	486	543	538	547	538	545	545
3d	465	462	422	463	474	465	506	513	511	515	507	506
3e	465	465	465	461	466	466	492	498	496	500	492	492
3f	465	465	460	465	486	465	490	495	494	497	491	491
3h	475	465	464	468	474	465	491	496	495	499	492	492
3i	466	465	465	441	486	466	495	496	497	499	498	498
3j	473	466	464	466	486	465	506	512	513	515	507	507
3k	466	466	468	465	487	465	492	495	495	497	494	494
31	479	465	466	475	475	465	495	497	497	499	497	496
3m	464	465	465	466	469	465	490	496	495	498	490	490

	3a	3b	3с	3d	3e	3f	3h	3i	3j	3k	31	3m
SCF energy (-a.u.) Zero point vib. energy (kcal mol ⁻¹)	1514,06688 245,00475	1514,07863 244,96032	1514,07893 244,9677	1348,83700 260,91642	1348,84187 260,5617	1348,84224 260,5567	1424,07002 263,65047	1424,07196 263,70517	1769,12726 237,39939	1769,13756 237,48339	1769,13758 237,48168	1309,51436 243,55635
Rotational constants (GHz)	0,19308	0,17595	0,19185	0,21265	0,20007	0,20703	0,18505	0,20378	0,20118	0,18393	0,19839	0,21643
	0,07076	0,06591	0,0528	0,07237	0,07193	0,06677	0,06626	0,05728	0,07045	0,06717	0,05703	0,07629
	0,05389	0,04833	0,04192	0,05464	0,05356	0,05102	0,0493	0,04513	0,05404	0,04968	0,04477	0,05702
E (thermal) kcal/mol	262,321	262,342	262,352	277,599	277,504	277,508	281,099	281,146	253,934	254,015	254,027	259,288
Specific heat (Cv) (cal mol ^{-1} K ^{-1})	107,408	107,468	107,429	104,662	104,988	104,969	108,219	108,206	102,749	102,732	102,717	98,864
Entropy (S) (cal mol ^{-1} K ^{-1})	188,384	191,462	192,695	183,361	187,885	187,736	191,757	190,876	183,624	185,311	185,527	176,598
Dipole moment (Debye)	4,7567	6,0223	11,5101	6,0388	6,0301	5,5387	5,3719	3,8061	5,4152	5,7943	7,306	5,9729

 Table 7
 Calculated thermodynamic parameters of 3a-3m at B3LYP/6-311++G(d,p) level.

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