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Synthesis and Absorption Properties of Trisubstituted Hetarylazo Indole Dyes

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Abstract: In this study, as a result of azo coupling of diazonium salts prepared with various aromatic amines with 2-(4-methylphenyl)-1*H*-indole and 2-(4-chlorophenyl)-1*H*-indole compounds, a series of new hetarylazo indole dyes were synthesized. *N*-substituted indole derivatives were synthesized by alkylation of the prepared dyes with the isopropyl alcohol from the *N*-position by Mitsunobu reaction. The chemical structures of the synthesized compounds were determined by NMR, FT-IR, UV-vis, mass spectrometry and elemental analysis. In order to determine the photophysical properties of the dyes obtained, visible region absorption spectra were examined in solvents of different polarity. In addition, the behavior of acid and base addition on absorption maxima were examined in detail.

Key words: Indole derivatives, Azo compounds, Mitsunobu alkylation, Solvent effect

Trisübstitüe Hetarilazo İndol Boyalarının Sentezi ve Absorpsiyon Özelliklerinin İncelenmesi

Özet: Bu çalışmada, çeşitli aromatik aminler ile hazırlanan diazonyum tuzlarının, 2-(4-metilfenil)-1*H*-indol ve 2-(4-klorfenil)-1*H*-indol bileşikleri ile azo kenetlenmesi sonucu, bir dizi yeni hetarilazo indol boyası sentezlendi. Hazırlanan boyarmaddelerin, Mitsunobu reaksiyonu ile *N*-pozisyonundan izopropil alkol ile alkillenmesi sonucu *N*-sübstitue indol türevlerinin sentezi gerçekleştirildi. Sentezlenen bileşiklerin kimyasal yapıları, NMR, FT-IR, UV-vis, kütle spektrometresi ve elementel analiz ile aydınlatıldı. Elde edilen boyarmaddelerin fotofiziksel özelliklerini belirlemek için, farklı polariteye sahip çözücüler içerisinde görünür bölge absorpsiyon spektrumları incelendi. Ek olarak, asit ve baz ilavesinin absorpsiyon maksimumları üzerine etkileri ayrıntılı olarak incelendi.

Anahtar kelimeler: İndol türevleri, Azo bileşikleri, Mitsunobu alkilasyonu, Çözücü etkisi

1. Introduction

Azo group-containing dyestuffs represent the most important synthetic colorant group and are the largest class of dyes used today. Many types of azo dyes are known commercially and about two-thirds of all synthetic dyes consist of dyes containing azo groups [1]. The use of these dyes dates back many years and is estimated to be at least 3000 azo dyes. These dyes are especially used in the pharmaceutical and paper industries and are also widely used in varnish and wood paints [2]. Azo compounds are a large and versatile class of dyes and represent for more than 50% of dye products produced worldwide [3]. Azo dyes derived from heterocyclic ring-containing molecules are worth examining for their superior properties. Heterocyclic diazo derivatives have been used generally in the synthesis of disperse dyes because they are brighter and have higher

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strength than azo dyes obtained from substituted aromatic amines. The absorption properties of these dyes are often influenced by solvents and exhibited bathochromism after increasing the polarity of the solvent [4-6].

Organic molecules containing indole groups are important compounds for natural product chemistry and pharmacology. Therefore, the search of new methods for the synthesis of indole-derived compounds is of interest to many chemists [7,8]. Indole was discovered by Baeyer and Knop in 1986 as the basic structure of natural dye indigo [9]. In the first published study on the coupling of diazonium salts with indole, it was found that 2-methylindole reacts rapidly with the diazonium salt to obtain a crystalline azo compound. Pauly and Gundermann then reported the reaction of diazotized sulfanilic acid with substituted indole derivatives [10]. In the literature, it is stated that some dyes are synthesized using indole and derivatives as heterocyclic coupling component [11-20].

In recent years, there many studies on the mechanism and applications of Mitsunobu reaction in the literature. This method was first reported by Mitsunobu and Yamada in 1967. The method has been described as a new reaction which forms a dehydrative bond between a carboxylic acid and a primary or secondary alcohol using a mixture of diethyl azodicarboxylate and triphenylphosphine [21]. In secondary alcohol substrats, it has been noted that this condensation reaction continues with the reversal of configuration at the alcohol center and leads to a general method for the preparation of such derivatives. Afterwards, the scope of this reaction mechanism and its applications on natural product synthesis have been extensively discussed and reviewed [22-24].

In this study, the preparation of a series of new bis-hetarylazo indole compounds was aimed. Then, we intended to find new knowledge to support these synthesized compounds in solution and solid state. In this context, we now report dyes using 2-(4-methyphenyl)-1*H*-indole and 2-(4-chlorophenyl)-1*H*-indole as coupling components which may be involved in azo-hydrazone tautomerism. 2-(4-methyphenyl)-1*H*-indole and 2-(4-chlorophenyl)-1*H*-indole compounds were synthesized according to literature method [25]. Diazotization of aniline derivatives and their subsequent coupling with 2-(4-methyphenyl)-1*H*-indole and 2-(4-chlorophenyl)-1*H*-indole gave a series of bis(hetaryl)monoazo disperse dyes. With the synthesized dyes alkylated with isopropyl alcohol from *N*-position by Mitsunobu reaction, *N*-substituted indole derivatives were synthesized. Then, we evaluated the UV-vis absorption spectra according to the effect of the solvent. Moreover, the influence of acid and base addition on the UV-vis absorption spectrum of the compounds has been reported.

2. Material and Method

2.1 General information

The chemicals and spectroscopic grade solvents used in the study were obtained from Aldrich and Merck Chemical Companies and were used without purification. FT-IR analysis was performed with Perkin Elmer Spectrum One spectrophotometer using KBr. NMR analysis were performed in deuterated chloroform ($CDCl_3$) using the Bruker 500 NMR spectrometer using tetramethylsilane (TMS) as the internal reference. Chemical shifts are reported in δ units (ppm). UV-Visible absorption spectra were recorded on Shimadzu UV-1700 Pharmaspec spectrophotometer at the wavelength of maximum absorption (λ_{max}) of dyes in a range of solvents, that is, dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetonitrile (ACN), methanol (MeOH), acetic acid (AcOH), and chloroform ($CHCl_3$) at various concentrations (approximately 1×10^{-6} to 1×10^{-8}). Change of λ_{max} was investigated when 0.1 mL potassium hydroxide solution (0.1 M in

methanol) or 0.1 mL hydrochloric acid solution (0.1 M in methanol) was added to 1 mL methanolic dye solutions. Mass spectra were recorded on Bruker Daltonics microTOF II ESI-TOF mass spectrometer. Elemental analyses (EA) were performed using a ThermoFinnigan FLASH 1112 SERIES EA instrument. Melting points were determined in open glass capillary tube by means of a BÜCHI Melting Point B-450 aparatus.

2.2 Synthesis of 2-phenylindoles

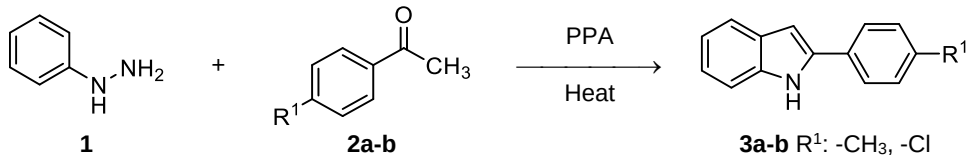

Figure 1. Synthesis of 2-substituted indoles

A mixture of phenylhydrazine (**1**, 5.95 g, 5.42 mL, 55.0 mmol, 1.00 eq) and acetophenone derivatives (**2a-b**, 55.0 mmol, 1.00 eq) was stirred at 60 °C for 30 min and then cooled to room temperature. To the reaction mixture, 20 g polyphosphoric acid was added portionwise and the reaction mixture was heated to 100 °C. After completion, the reaction mixture cooled to room temperature, stirred with 50 mL of cold water for about 30 min. and filtrated. The product was recrystallized from ethanol/water mixture.

2.3 Synthesis of hetarylazo indole dyes (5a-f)

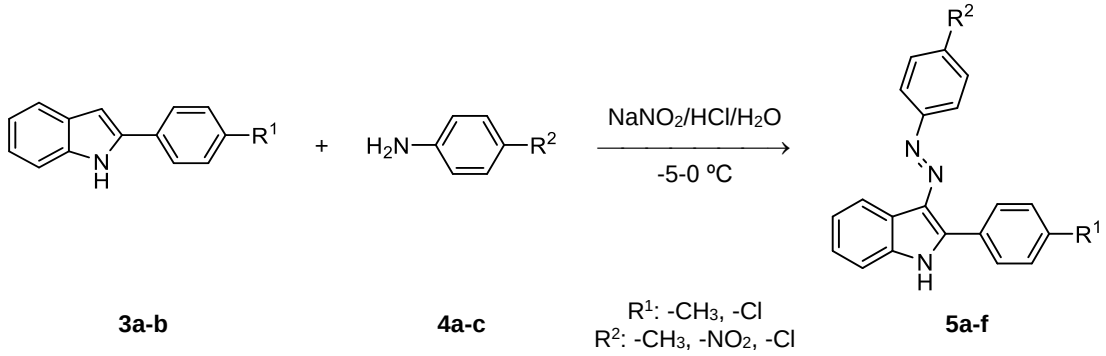

Figure 2. Synthesis of 2,3-disubstituted indoles

2.3.1 2-(4-methylphenyl)-3-[(4-methylphenyl)diazenyl]-1H-indole (5a)

4-methylaniline (**4a**, 1.50 g, 1.54 mL, 14.0 mmol, 1.00 eq) was dissolved in HCl (3.75 mL) and water (3.30 mL) mixture. The solution was cooled to 0 °C via an ice-salt bath and a cold solution of $NaNO_2$ (0.98 g, 14.0 mmol, 1.00 eq) in water (5.7 mL) was added dropwise to the mixture. A solution of 2-(4-methylphenyl)-1*H*-indole (**3a**, 2.90 g, 14.0 mmol, 1.00 eq) in 100 mL of ethanol was added dropwise to a diazonium salt solution cooled to 0 °C. The solution was stirred at -5–0 °C for 1 hour and the resulting solid was filtrated, washed with cold water and dried. The product was obtained as an orange crystal after recrystallization in ethanol (**5a**, 4.19 g, 12.9 mmol, 92%). **Mp**: 148–149 °C. **FT-IR** (KBr): ν_{max} = (–*N*H): 3412–3308 cm^{-1}; (Ar. C–H): 3011 cm^{-1}; (Aliph. C–H): 2918-2846 cm^{-1}; (C=C): 1456 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.54 (bs, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.40-7.32 (m, 4H), 7.19-7.11 (m, 4H), 2.42 (s, 3H), 2.36 (s, 3H). **MS** (ESI+): ($[M+H]^+$)(m/z): 326.1696. **EA**: Calcd for $C_{22}H_{19}N_3$: C, 81.20; H, 5.89; N, 12.91. Found: C, 79.40; H, 6.49; N, 14.11.

2.3.2 2-(4-methylphenyl)-3-[(4-nitrophenyl)diazenyl]-1H-indole (5b)

The product was obtained as dark red crystals (**5b**, 4.21 g, 11.8 mmol, 84%). **Mp**: 196–199 °C. **FT-IR** (KBr): ν_{max} = (–*N*H): 3352 cm^{-1}; (Ar. C–H): 3035 cm^{-1}; (Aliph. C–H): 2918–2851 cm^{-1}; (C=C): 1319 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.62 (bs, 1H), 8.33 (d, *J* = 8.7 Hz, 2H), 7.96-7.91 (m, 4H), 7.59-7.54 (m, 2H), 7.36-7.34 (m, 4H) 2.45 (s, 3H). **MS** (ESI+): ($[M+H]^+$)(m/z): 357.1306. **EA**: Calcd for $C_{21}H_{16}N_4O_2$: C, 70.77; H, 4.53; N, 15.72. Found: C, 70.23; H, 3.78; N, 16.13.

2.3.3 2-(4-methylphenyl)-3-[(4-chlorophenyl)diazenyl]-1H-indole (5c)

The product was obtained as orange crystals (**5c**, 4.25 g, 12.3 mmol, 88%). **Mp**: 162–164 °C. **FT-IR** (KBr): ν_{max} = (–*N*H): 3407 cm^{-1}; (Ar. C–H): 3034 cm^{-1}; (Aliph. C–H): 2932–2857 cm^{-1}; (C=C): 1368 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.55 (bs, 1H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.42-7.37 (m, 4H), 7.25-7.17 (m, 4H), 2.38 (s, 3H). **MS** (ESI+): ($[M+H]^+$)(m/z): 346.1082. **EA**: Calcd for $C_{21}H_{16}ClN_3$: C, 72.93; H, 4.66; N, 12.15. Found: C, 72.21; H, 4.57; N, 10.97.

2.3.4 2-(4-chlorophenyl)-3-[(4-methylphenyl)diazenyl]-1H-indole (5d)

The product was obtained as orange crystals (**5d**, 4.59 g, 13.2 mmol, 94%). **Mp**: 184–186 °C. **FT-IR** (KBr): ν_{max} = (–*N*H): 3398 cm^{-1}; (Ar. C–H): 3046 cm^{-1}; (Aliph. C–H): 2927–2858 cm^{-1}; (C=C): 1486 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.54 (bs, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.42-7.38 (m, 4H), 7.31-7.29 (m, 4H), 2.44 (s, 3H). **MS** (ESI+): ($[M+H]^+$)(m/z): 346.1117. **EA**: Calcd for $C_{21}H_{16}ClN_3$: C, 72.93; H, 4.66; N, 12.15. Found: C, 70.43; H, 4.37; N, 11.86.

2.3.5 2-(4-chlorophenyl)-3-[(4-nitrophenyl)diazenyl]-1H-indole (5e)

The product was obtained as dark red crystals (**5e**, 4.78 g, 12.7 mmol, 91%). **Mp**: 276–278 °C. **FT-IR** (KBr): ν_{max} = (–*N*H): 3376 cm^{-1}; (Ar. C–H): 3105 cm^{-1}; (Aliph. C–H): 2872 cm^{-1}; (C=C): 1332 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.95 (bs, 1H), 8.36 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.61-7.54 (m, 4H), 7.48-7.44 (m, 4H). **MS** (ESI+): ($[M+H]^+$)(m/z): 377.0596. **EA**: Calcd for $C_{20}H_{13}ClN_4O_2$: C, 63.75; H, 3.48; N, 14.87. Found: C, 64.51; H, 4.02; N, 14.42.

2.3.6 2-(4-chlorophenyl)-3-[(4-chlorophenyl)diazenyl]-1H-indole (5f)

The product was obtained as orange crystals (**5f**, 4.65 g, 12.7 mmol, 91%). **Mp**: 177–178 °C. **FT-IR** (KBr): ν_{max} = (–*N*H): 3406 cm^{-1}; (Ar. C–H): 3071 cm^{-1}; (Aliph. C–H): 2927–2833 cm^{-1}; (C=C): 1489 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.64 (bs, 1H), 8.60 (d, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.51 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.33-7.31 (m, 3H). **MS** (ESI+): ($[M+H]^+$)(m/z): 366.04. **EA**: Calcd for $C_{20}H_{13}Cl_2N_3$: C, 65.59; H, 3.58; N, 11.47. Found: C, 64.72; H, 3.92; N, 10.98.

2.4 Synthesis of N-substituted indoles (7a-f)

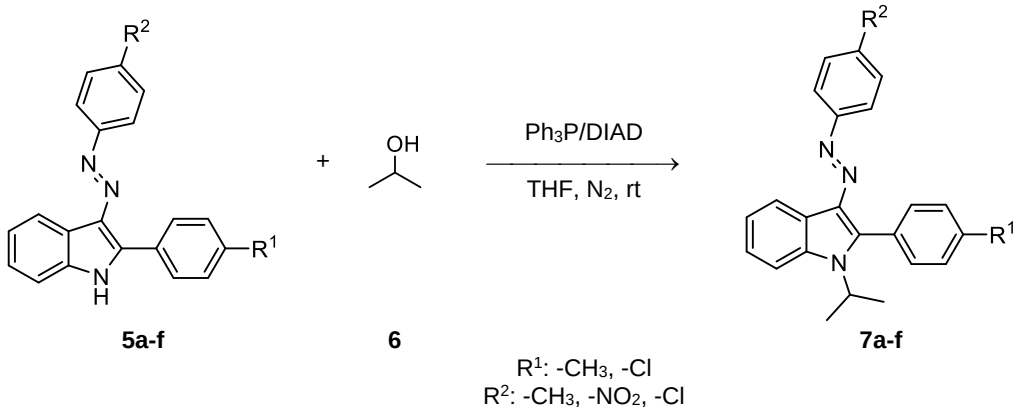

Figure 3. Synthesis of *N*-substituted indoles

2.4.1 1-isopropyl-3-[(4-methylphenyl)diazenyl]-2-(4-methylphenyl)-1H-indole (7a)

To a solution of 2-(4-methylphenyl)-3-[(4-methylphenyl)diazenyl]-1*H*-indole) (**5a**, 0.5 g, 1.54 mmol, 1.00 eq) in dry THF (10 mL) was added triphenylphosphine (0.8 g, 3.08 mmol, 2.00 eq), 2-propanol (**6**, 590 µL, 462 mg, 7.70 mmol, 5.00 eq) and diisopropyl azodicarboxylate (DIAD, 910 µL, 934 mg, 4.62 mmol, 3.00 eq). The reaction mixture was stirred at room temperature for 1 h and followed by thin layer chromatography. After completion, the mixture was diluted with sodium carbonate solution and the resulting mixture was extracted with 3 x 20 mL of ethyl acetate and dried over Na_2SO_4. Then removing all volatile components by rotary evaporation under reduced pressure, the product **(7a)** was obtained as orange solid (240 mg, 43%) via column chromatographic purification on silica gel. **Mp**: 130–131 °C. $\mathbf{R_f}$ = 0.82 (silica gel; hexane/$CHCl_3$, 1:1). **FT-IR** (KBr): ν_{max} = (Ar. C–H): 3024 cm^{-1}; (Aliph. C–H): 2973–2919 cm^{-1}; (C=C): 1453 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.67-7.60 (m, 5H), 7.48-7.43 (m, 2H), 7.35-7.30 (m, 5H), 4.85-4.79 (m, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 1.67 (d, *J* = 7.0 Hz, 6H). **^{13}C-NMR** (APT, 125 MHz, $CDCl_3$): δ = 146.2 (C), 138.8 (C), 138.4 (C), 134.9 (C), 131.3 (CH), 129.4 (CH), 128.7 (CH), 127.7 (C), 123.6 (CH), 123.2 (CH), 122.7 (CH), 121.8 (CH), 120.2 (C), 113.3 (CH), 112.3 (CH), 48.7 (CH), 21.5 (CH_3), 21.4 (CH_3). **MS** (ESI+): ($[M+H]^+$)(m/z): 368.1970. **EA**: Calcd for $C_{25}H_{25}N_3$: C, 81.71; H, 6.86; N, 11.43. Found: C, 80.06; H, 6.76; N, 10.46.

2.4.2 1-isopropyl-3-[(4-nitrophenyl)diazenyl]-2-(4-methylphenyl)-1H-indole (7b)

The product was obtained as red solid (**7b**, 210 mg, 0.59 mmol, 38%). **Mp**: 127–128 °C. $\mathbf{R_f}$ = 0.59 (silica gel; hexane/$CHCl_3$, 1:1). **FT-IR** (KBr): ν_{max} = (Ar. C–H): 2981 cm^{-1}; (Aliph. C–H): 2935 cm^{-1}; (C=C): 1365 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.79-7.67 (m, 5H), 7.48-7.6 (m, 2H), 7.39-7.36 (m, 5H), 4.89-4.83 (m, 1H), 2.51 (s, 3H) 1.71 (d, *J* = 7.0 Hz, 6H). **^{13}C-NMR** (APT, 125 MHz, $CDCl_3$): δ = 161.1 (C), 158.2 (C), 149.6 (C), 139.6 (C), 135.2 (C), 131.1 (CH), 129.0 (CH), 127.0 (C), 124.6 (CH), 124.1 (CH), 123.8 (CH), 123.7 (CH), 122.1 (CH), 119.8 (C), 113.3 (CH), 112.7 (CH), 49.2 (CH), 21.6 (CH_3), 21.5 (CH_3). **MS** (ESI+): ($[M+H]^+$)(m/z): 399,1653. **EA**: Calcd for $C_{24}H_{22}N_4O_2$: C, 72.34; H, 5.57; N, 14.06. Found: C, 71.42; H, 5.83; N, 14.36.

2.4.3 1-isopropyl-3-[(4-chlorophenyl)diazenyl]-2-(4-methylphenyl)-1H-indole (7c)

The product was obtained as orange solid (**7c**, 220 mg, 0.60mmol, 39%). **Mp**: 137–140 °C. $\mathbf{R_f}$ = 0.84 (silica gel; hexane/$CHCl_3$, 1:1). **FT-IR** (KBr): ν_{max} = (Ar. C–H): 3044 cm^{-1}; (Aliph. C–H): 2973–2934 cm^{-1}; (C=C): 1378 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 4H), 7.48-7.47 (m, 2H), 7.35-7.31 (m, 6H) 4.85-4.80 (m, 1H), 2.49 (s, 3H), 1.68 (d, *J* = 7.0 Hz, 6H). **^{13}C-NMR** (APT, 125 MHz, $CDCl_3$): δ = 152.9 (C), 147.2 (C), 139.0 (C), 135.0 (C), 133.7 (C), 131.2 (CH), 128.9 (CH), 128.8 (CH), 127.4 (C), 123.5 (CH), 123.0 (CH), 120.1 (C), 113.3 (CH), 112.5 (CH), 48.8 (CH), 21.5 (CH_3), 21.4 (CH_3). **MS** (ESI+): ($[M+H]^+$)(m/z): 388,1401. **EA**: Calcd for $C_{24}H_{22}ClN_3$: C, 74.31; H, 5.72; N, 10.83. Found: C, 75.06; H, 5.82; N, 10.40.

2.4.4 1-isopropyl-3-[(4-methylphenyl)diazenyl]-2-(4-chlorolphenyl)-1H-indole (7d)

The product was obtained as orange solid (**7d**, 280 mg, 0.79 mmol, 51%). **Mp**: 174–176 °C. $\mathbf{R_f}$ = 0.79 (silica gel; hexane/$CHCl_3$, 1:1). **FT-IR** (KBr): ν_{max} = (Ar. C–H): 3046 cm^{-1}; (Aliph. C–H): 2972–2935 cm^{-1}; (C=C): 1355 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.65-7.62 (m, 4H), 7.52 (s, 4H), 7.33-7.31 (m, 2H) 7.22-7.20 (m, 2H), 4.79-4.73 (m, 1H), 2.38 (s, 3H), 1.68 (d, *J* = 6.9 Hz, 6H). **^{13}C-NMR** (APT, 125 MHz, $CDCl_3$): δ = 152.3 (C), 144.4 (C), 138.8 (C), 135.1 (C), 135.0 (C), 132.7 (CH), 129.5 (CH), 128.3 (CH), 123.7 (CH), 123.6 (CH), 122.9 (CH), 121.8 (CH), 120.1 (C), 113.3 (C), 112.4 (CH), 48.9 (CH), 21.6 (CH_3), 21.3 (CH_3). **MS** (ESI+): ($[M+H]^+$)(m/z): 388,1382. **EA**: Calcd for $C_{24}H_{22}ClN_3$: C, 74.31; H, 5.72; N, 10.83. Found: C, 75.06; H, 5.75; N, 10.03.

2.4.5 1-isopropyl-3-[(4-nitrophenyl)diazenyl]-2-(4-chlorolphenyl)-1H-indole (7e)

The product was obtained as red solid (**7e**, 350 mg, 0.97 mmol, 63%). **Mp**: 140–141 °C. $\mathbf{R_f}$ = 0.57 (silica gel; hexane/$CHCl_3$, 1:1). **FT-IR** (KBr): ν_{max} = (Ar. C–H): 3055 cm^{-1}; (Aliph. C–H): 2970–2934 cm^{-1}; (C=C): 1381 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 8.7 Hz, 2H), 7.79-7.77 (m, 2H), 7.57-7.51 (m, 6H), 7.39-7.37 (m, 2H) 4.82-4.77 (m, 1H), 1.71 (d, *J* = 7.0 Hz, 6H). **^{13}C-NMR** (APT, 125 MHz, $CDCl_3$): δ = 160.4 (C), 159.5 (C), 148.8 (C), 139.3 (C), 136.2 (C), 132.4 (CH), 128.6 (CH), 126.8 (C), 124.7 (CH), 124.4 (CH), 124.0 (CH), 123.7 (CH), 122.1 (CH), 119.9 (C), 113.2 (CH), 112.8 (CH), 49.4 (CH), 21.5 (CH_3). **MS** (ESI+): ($[M+H]^+$)(m/z): 419.1121. **EA**: Calcd for $C_{23}H_{19}ClN_4O_2$: C, 65.95; H, 4.57; N, 13.38. Found: C, 65.77; H, 4.69; N, 13.93.

2.4.6 1-isopropyl-3-[(4-chlorophenyl)diazenyl]-2-(4-chlorolphenyl)-1H-indole (7f)

The product was obtained as orange solid (**7f**, 310 mg, 0.85 mmol, 55%). **Mp**: 176–178 °C. $\mathbf{R_f}$ = 0.91 (silica gel; hexane/$CHCl_3$, 1:1). **FT-IR** (KBr): ν_{max} = (Ar. C–H): 3053 cm^{-1}; (Aliph. C–H): 2970–2934 cm^{-1}; (C=C): 1374 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 4H), 7.55-7.50 (m, 4H), 7.38-7.33 (m, 4H), 4.79-4.73 (m, 1H), 1.68 (d, *J* = 7.0 Hz, 6H). **^{13}C-NMR** (APT, 125 MHz, $CDCl_3$): δ = 152.7 (C), 142.3 (C), 134.1 (C), 132.6 (CH), 129.0 (CH), 128.4 (CH), 127.2 (CH), 123.8 (CH), 123.6 (CH), 123.2 (CH), 123.0 (CH), 119.9 (C), 113.3 (C), 112.5 (CH), 49.0 (CH), 21.5 (CH_3). **MS** (ESI+): ($[M+H]^+$)(m/z): 408.0877. **EA**: Calcd for $C_{23}H_{19}Cl_2N_3$: C, 67.65; H, 6.69; N, 10.29. Found: C, 67.42; H, 6.82; N, 10.11.

3. Results

3.1. Spectral properties and tautomerism

Hetarylazo indole derivatives **5a-f** were prepared by coupling 2-(4-methyphenyl)-1*H*-indole and 2-(4-chlorophenyl)-1*H*-indole with diazotized heterocyclic amines in nitrosyl acid. *N*-substituted indole derivatives (**7a-f**) were synthesized by Mitsunobu reaction. The structure of prepared compounds was characterized by elemental analysis and spectroscopic methods (FT-IR, Mass and ^{1}H-NMR). When the infrared spectra of these dyes containing indole ring (**5a-f**) were examined, a weak and wide band in the range of 3388-3210 cm^{-1} was observed due to –*N*H band in the structure. These bands were not observed in the infrared spectra of the *N*-substituted indole dyes (**7a-f**). The other peak values at 3085–3005 cm^{-1} (aromatic CH) and at 2986–2851 cm^{-1} (aliphatic CH) were recorded. ^{1}H NMR spectra of the dyes (**5a-f**) showed –*N*H peaks in the range 8.36–8.62 ppm in $CDCl_3$. These peaks were not observed in the NMR spectra of the *N*-substituted indole compounds (**7a-f**). The other δ values 2.28–2.40 ppm (CH_3) and 8.35–6.98 ppm (aromatic H) were recorded. These results show that compounds **5a-f**, **7a-f** are in single tautomeric (azo; −N=N−) form in $CDCl_3$ and solid state.

3.2. Solvent effects

Table 1 shows the UV-vis absorption values of 10^{-6}–10^{-8} M solutions of the compounds (**5a-f, 7a-f**) synthesized in different solvents measured in the range of 350-550 nm. The visible absorption spectra of the dyes did not correlate with the polarity of solvent. For all compounds synthesized according to these values, a single maximum peak is seen in all solvents.

Table 1 Influence of solvent on λ_{max} (nm) of dyes **5a-f**, **7a-f**

Dye no	DMSO	DMF	ACN	MeOH	AcOH	$CHCl_3$
5a	402	399	394	395	394	392
5b	461	455	440	445	438	441
5c	407	405	399	401	399	397
5d	401	399	393	394	393	392
5e	459	451	435	439	434	438
5f	407	405	348	399	398	397
7a	392	389	386	383	383	390
7b	451	442	435	432	431	440
7c	397	394	388	390	390	393
7d	389	386	384	382	383	385
7e	442	436	431	426	426	433
7f	395	393	390	388	388	390

When the graph in Figure 4 is examined, it is seen that all synthesized dyes (**5a-f**, **7a-f**) have a single absorbance value in all solvents. This result indicates that the dyes **5a-f**, **7a-f** are present in a single tautomeric form in all solvents (DMSO, DMF, ACN, MeOH, AcOH, and $CHCl_3$). It was observed that all indole derivative dyes synthesized were subjected to bathochromic shift of absorption maxima in DMSO and DMF. In addition, for dye **7b**, a bathochromic shift in DMSO, DMF and chloroform, and hypsochromic shift in methanol and acetic acid for dye **7e**, were observed.

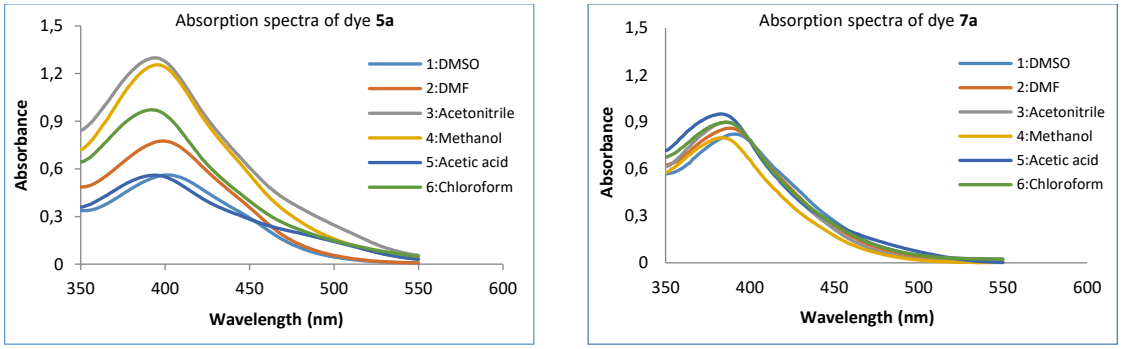

Figure 4. Absorption spectra of dye **5a** and **7a** in different solvents

3.3. Acid and base effects

Table 2 shows the change of maximum absorption values of the compounds (**5a-f**, **7a-f**) by adding acid-base into methanol. When the acid and base effects on the absorption spectra of the synthesized compounds were evaluated, it was observed that the absorption spectra of all the compounds except the **5f** compound did not change with the addition of acid and base. When 0.1 M potassium hydroxide solution is added to the solution of compound **5f** in MeOH, the absorption band shows a hypsochromic shift relative to the absorption band in methanol. In addition of 0.1 M hydrochloric acid solution, no change in absorption maximum is observed.

Table 2 Absorption data of dyes **5a-f**, **7a-f** in acidic and basic solutions

Dye no	λ_{max} (nm)			Dye no	λ_{max} (nm)		
	MeOH	MeOH +KOH	MeOH +HCl		MeOH	MeOH +KOH	MeOH +HCl
5a	395	394	397	**7a**	383	384	383
5b	445	446	445	**7b**	432	433	435
5c	401	400	401	**7c**	390	391	391
5d	394	393	394	**7d**	382	383	383
5e	439	443	440	**7e**	426	428	429
5f	399	384	399	**7f**	388	389	389

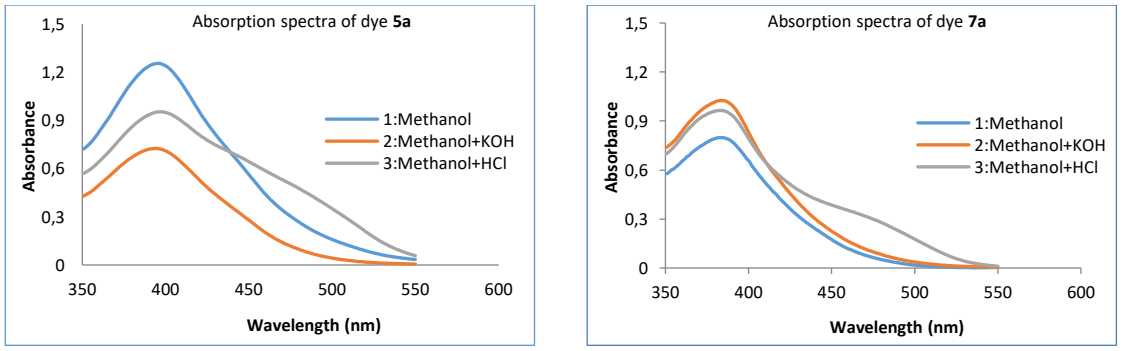

Figure 5. Absorption spectra of dye **5a** and **7a** in acidic and basic solutions

4. Conclusion and Comment

In this study, two different 2-substituted indole derivatives synthesized using Fischer indole synthesis method. Compounds (**3a-b**) were synthesized in accordance with the literature [25]. In the next step of the study, 6 new hetarylazo indole dyes were

synthesized by coupling diazonium salts obtained by diazonization of various aromatic amines with 2-(4-methylphenyl)-1*H*-indole (**3a**) and 2-(4-chlorophenyl)-1*H*-indole (**3b**) compounds. The structures of the synthesized compounds (**5a-f**) were characterized by NMR, FT-IR, mass spectrometry and elemental analysis. Of these molecules, for the compound **5f**, the ^{1}H-NMR results given in the literature, the structure is stated to contain 12 protons [26]. However, according to our ^{1}H-NMR results, it was found that **5a-f** compounds contain 13 protons together with -*N*H proton in indole ring.

Visible absorption spectra of the synthesized dyes in different solvents were examined. Compounds **5a-f** in DMSO, DMF, ACN, MeOH, AcOH and $CHCl_3$ absorption spectra were examined when it was observed that they have a single λ_{max} values, the compounds are thought to be in one form. In this case, it is thought that there is no tautomerism. In addition, when 0.1 M potassium hydroxide and 0.1 M hydrochloric acid solutions were added to the solutions of the compounds in methanol, a single maximum value was observed in the absorption spectrum and this group of compounds were not sensitive to acid and base addition.

Finally, 6 new *N*-substituted indole derivatives were synthesized by alkylating 2,3-disubstituted indole dyes from *N* position with isopropyl alcohol by Mitsunobu reaction. The structures of the synthesized compounds (**7a-f**) were characterized by NMR, FT-IR, mass spectrometry and elemental analysis.

Visible absorption spectra of the synthesized dyes in different solvents were investigated. When the absorption spectra of compounds **7a-f** were examined in DMSO, DMF, ACN, MeOH, AcOH and $CHCl_3$, they were found to have single λ_{max} values and accordingly the compounds were considered to be in single form. In this case, it is thought that there is no tautomerism. In addition, when 0.1 M potassium hydroxide and 0.1 M hydrochloric acid solutions were added to the solutions of the compounds in methanol, a single maximum value was observed in the absorption spectrum and these compounds were not sensitive to acid and base addition.

Author Statement

Mehmet Ulutürk: Investigation, Original Draft Writing, Review and Editing.
Tahir Tilki: Investigation, Review and Editing, Supervision, Observation, Advice.

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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