

SYNTHESIS OF SOME AZO DYES BASED
ON 2,3,3-TRIMETHYL-3H-INDOLENINETinatin Bukia^{1, ✉}, Mariam Utiashvili², Manana Tsiskarishvili², Sopo Jalalishvili²,
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Abstract. New azo compounds on the base of 2,3,3-trimethyl-3H-indolenine were synthesized and characterized by FT-IR, NMR, and Mas-spectral analysis. The synthesis was conducted in three different pathways: 1) by reducing the nitro compound with Zn/NaOH in alcohol; 2) by heating of 2,3,3-trimethyl-3H-indolenine-5-amine in the presence of MnO₂ in toluene, and 3) by diazotization of 2,3,3-trimethyl-3H-indolenine-5-amine and treating the resulting diazonium salt with the appropriate coupler.

Keywords: azo dyes, bis azo dye, reduction, 2,3,3-trimethyl-3H-indolenine, synthesis.

1. Introduction

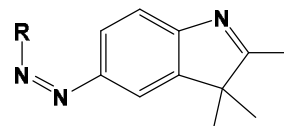
Azo dyes are the largest group of dye chemistry today. They occupy a special place in terms of their use. The area of application of azo dyes is mainly limited to the textile, leather, and plastics industries, printing market, paper manufacturing,¹ bio-medical studies, non-linear optical systems, photochromic materials, sensors, and photo-sensitizers, molecular photoswitches, molecular machines, linkers in biological macromolecules, guests in inclusion complexes, surfactants, ligands, polymers, liquid crystals.²⁻¹⁵ The pharmacologic effect of these compounds has also been identified, which has led to their widespread use in medicine as antitumor, antifungal, antibacterial, and antioxidant activities.¹⁶⁻²²

Azo-compounds are derivatives by one or more nitrogen-nitrogen double bonds -N=N-, where nitrogen atoms are connected respectively to *sp*²-hybridized carbon

atoms. Azo-compounds are expressed by the following formula: Ar-N=N-R. The -N=N- chromophore group, as the electron-withdrawing group is principally responsible for the color observed.²³⁻³⁰

The synthesis of azo dyes is distinguished by their simplicity, which takes place in acid and alkaline conditions, with the interaction of weak electrophiles (aryl diazonium ion) and strong nucleophiles (activated aromatic compound). The first stage involves N-nitrosation (diazotization) of aromatic amines to diazonium salt in a mineral acid area at low temperature, and the second stage takes place by coupling the diazonium ion to an electron-rich aromatic ring via an electrophilic aromatic substitution reaction. The first step requires control to avoid side effects, formation of self-coupling product, or decomposition of the diazonium ion. After the coupling reaction, the azo group bonded to the nucleophiles and yielded a desired colored product.²³⁻³⁰

In this study, we used three different pathways to synthesize new azo compounds (Scheme 1), including the classical way of syntheses, such as diazotization of amine at low temperature and subsequent coupling of the resulting diazo salt with a coupler, also, reducing the nitro compound by boiling in Zn dust in an alkaline solution, and by heating the amine with MnO₂ in toluene.³¹⁻³⁴



Scheme 1. General formula of azo dyes based on 2,3,3-trimethyl-3H-indolenine

The structures of obtained compounds were established using UV-Vis, FT-IR, NMR, and LC-MS analysis.

2. Experimental

2.1. Materials

All reagents used for synthesis were purchased from commercial suppliers (HCl, H₂SO₄, NaNO₂, MnO₂,

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methyl isopropyl ketone, and Zn-dust were purchased from Sigma-Aldrich; hexane, ethyl acetate, and methanol were purchased from Merck) and the purification according to standard literature methods (distillation) was done.

2,3,3-trimethyl-3H-indolenine (3). 102 g (1.04 mol, 56 mL) of 96% sulfuric acid were placed in a small portion in a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, dropping funnel, thermometer, and an ice bath with 390 g of ice. 108 g (1.0 mol, 98.5 mL) of phenylhydrazine (**1**) were added to the flask through the dropping funnel under stirring and cooling at 273-293 K. Then methyl-isopropyl ketone (**2**) in the amount of 92.5 g (1.0 mol, 115 mL) was added dropwise to the mixture in over 55 minutes and the reaction mixture was stirred and heated for three hours to 363 K. After finishing the reaction, the mixture was neutralized with a 100 mL of 50% sodium hydroxide solution up to pH 9. The mixture was transferred to a separatory funnel and the oil layer was separated. The aqueous layer was extracted two times with 150 mL of diethyl ether. The ether extract was dried over magnesium sulfate, then concentrated in the vacuum, and obtained oil was distilled at 502-503 K. 2,3,3-trimethyl-3H-indolenine (**3**) as a yellowish oil was obtained with a yield of 83%.³¹

2,3,3-trimethyl-5-nitro-3H-indolenine (4). 50 mL (92 g, 0.93 mol) of 96% sulfuric acid were placed in a 250 mL four-necked flask equipped with a mechanical stirrer, condenser, dropping funnel, thermometer, and ice bath. 20 g (0.1256 mol, 20.16 mL) of 2,3,3-trimethyl-3H-indolenine (**3**) were added dropwise through the dropping funnel under stirring and cooling, maintaining the temperature below about 333 K. When the solution was cooled to 293 K a "nitration mixture" of nitric acid/sulfuric acid in 1/4 ratio (7.56 g, 4.967 mL, 0.12 mol of nitric acid in 47 g, 0.48 mol, 25.58 mL of concentrated sulfuric acid) was slowly added by dropwise under vigorous stirring, maintaining the temperature up to 298 K. The mixture was stirred for more than two hours at room temperature and left overnight. The reaction was monitored by TLC. After the reaction, it was poured into cold water, or ice, and caustic soda was added in a small portion until pH 9. The formed nitro product was completely precipitated. The precipitate was filtered off, washed until neutral, and dried up. The product was purified by recrystallization from ethanol/water and a yellow powder³² was obtained with m.p. 402-403 K (lit. 403-404 K). IR spectrum, wavenumber, cm^{-1} : 3093, 1599 (C-H Aromatic), 2974, 1465-1449 (Methyl C-H asym. Stretch), 1514, 1334 (C-NO₂), 1314 (aromatic tertiary amine CN stretch); ¹H NMR (400 MHz, CDCl₃, δ ppm): 1.33 (6H, s, 2CH₃); 2.30 (3H, s, CH₃); 7.64-66 (1H, d, J=8.5 Hz, Ar); 8.23 (1H, dd, J=8.5, J=2.4 Hz, Ar); 8.41-8.35 (1H, m, Ar); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 16.1 (1C, CH₃); 22.4 (2C, CH₃); 54.79 (1C); 118 (1C, Ar); 120.2 (1C, Ar); 124.8 (2C, Ar); 145.5 (1C, Ar); 147.7 (1C, Ar); 159 (1C, Ar);

2,3,3-trimethyl-3H-indolenine-5-amine (5). A 150 mL three-necked flask equipped with a reflux condenser, thermometer, and heating mantle was loaded with 11 g (0.2 mol) of iron powder and 45 mL of 7% acetic acid. The flask was heated to 343-353 K for 15 min. Then a hot solution of 10 g (50 mmol) of 2,3,3-trimethyl-5-nitro-3H-indolenine (**4**) in 100 mL of ethanol was added in portions to the reaction mixture. The mixture was boiled for 1 h. After finishing the reaction 6 g (56.6 mmol) of sodium carbonate were added and the mixture was stirred for 10 min. The mixture was cooled, and the precipitate was filtered off and then washed with hot ethanol. It was concentrated in a rotary evaporator. The formed precipitate was filtered and recrystallized from aqueous ethanol (2:1). M.p. 451-452 K (lit. 451 K).³⁴ IR spectrum, wavenumber, cm^{-1} : 3317, 3188 (aromatic primary amine, NH stretch); 2957, 2922, 2861, 1473-1423 (methyl C-H asym/sym. stretch), 1647, 1615 (primary amine, NH bend), 1376, 1344 (aromatic tertiary amine, CN stretch), 3019 (C-H aromatic ring stretch); ¹H NMR (400 MHz, CDCl₃, δ ppm): 1.03 (3 H, s, CH₃); 1.16 (3H, s, CH₃); 2.1(3H, s, CH₃); 4.97 (2H, s, NH₂), 7.62(1H, d, j=8.1 Hz, Ar), 8.96 (1H, d, J=1.9 Hz, Ar), 8.51(1H, s, Ar); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 15.84 (2C, CH₃); 22.87 (1C, CH₃); 40.74 (1C); 113.8 (1C, Ar); 120.7 (1C, Ar); 121.9 (1C, Ar); 129.18 (2C, Ar); 155.0 (1C, Ar); 163.0 (1C, Ar);

1,2-bis(2,3,3-trimethyl-3H-indol-5-yl)-diazene (6). **Method A.** A 150 mL three-necked flask equipped with a reflux condenser, magnetic stirrer, and heating mantle was loaded with 1.25 g (31.25 mmol) of NaOH in 5 mL water and 2 g (10 mmol) of 2,3,3-trimethyl-5-nitro-3H-indolenine (**4**) in 5 mL ethanol. 1.47 g (22.5 mmol) of Zn dust were added in small portions under heating and stirring and an additional 15 mL of ethanol was poured into the flask, then it was heated to a boil. The reaction mixture got red. It was filtrated using a Buchner funnel and formed Zn(ONa)₂; unreacted Zn dust was washed up with 10 mL of hot ethanol. The filtrate was cooled and concentrated in a vacuum. The formed precipitate was filtered, washed up with water until neutral, and dried in the vacuum. 1,2-bis(2,3,3-trimethyl-3H-indol-5-yl)-diazene (**6**) was obtained as a dark orange powder. IR spectrum, wavenumber, cm^{-1} : 2961, 2925, 2858 (methyl C-H asym/sym. stretch); 1586-1473 (open-chain azo (-N=N-)), 1376, 1344 (aromatic tertiary amine CN stretch), 3050 (C-H aromatic ring stretch); ¹H NMR (400 MHz, CDCl₃, δ ppm): 1.13 (3H, s, CH₃); 1.37 (3H, s, CH₃); 1.48 (3H, s, CH₃); 7.05-7.07(1H, d, j=8.6 Hz, Ar), 8.09-8.10 (1H, d, J=2.3 Hz, Ar), 8.14-8.16 (1H, dd, j=8.7, 2.3 Hz, Ar); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 21.6 (2C, CH₃); 25.0 (1C, CH₃); 42 (1C), 118.9 (1C, Ar); 125.2 (1C, Ar); 142.5 (1C, Ar); 148.7 (2C, Ar); 159 (1C, Ar); 165 (1C, Ar); LC-MS, m/z (Irel, %): Found 344.3524 [M+1] (100%), Calculated m/z: 344.2001.

Method B. A 100 mL three-necked flask equipped with a reflux condenser, thermometer, and heating mantle was loaded with 0.5 g (2.9 mmol) of 2,3,3-trimethyl-3H-indolenine-5-amine (**5**) in 20 mL of toluene and 1.2 g (14.5 mmol) of manganese(IV) dioxide were added. The mixture was refluxed for 15 h with water removal (Dean-Stark) and then the formed suspension was filtered, washed several times with toluene, and the filtrate was evaporated in a vacuum to give a dark orange solid (**6**). It was recrystallized from methanol.

General Experimental Procedure of Diazotization (8a, b) method A:

A mixture of 1 g (5.74 mmol) of 2,3,3-trimethyl-3H-indolenine-5-amine (**5**) in 2.3 mL of 32% HCl and 2.3 mL of water were placed in a 100 mL beaker equipped with a magnetic stirrer. The clear solution was drowned in an ice bath and was diazotized with 0.349 g (5.74 mmol) of sodium nitrite dissolved in 1.43 mL of water at 273-282 K. To the clear diazo solution 0.54 g (5.74 mmol) of phenol (**1**) in 21.5 mL of water, 0.2296 g (5.74 mmol) of sodium hydroxide and 2.12 g (20 mmol) of sodium carbonate were added at a low temperature in a small portion. The mixture was stirred at room temperature overnight. Then it was filtered off and washed with a 10% of sodium chloride solution. The obtained sediment suspension in water is then acidified to a weak acid reaction by adding hydrochloric acid. After that, the obtained precipitate was filtered, washed up to neutral with water, and dried.

4-((2,3,3-trimethyl-3H-indol-5-yl)diazenyl)phenol (8a): IR spectrum, wavenumber, cm^{-1} : 3254 (phenolic OH stretch), 3030 (C-H aromatic ring stretch), 2923 (methyl C-H asym /sym. stretch), 1592-1474 (open-chain azo (-N=N-)), 1386, 1346 (aromatic tertiary amine CN stretch); ^1H NMR (400 MHz, CDCl_3 , δ ppm): 1.20 (3H, m, CH_3), 1.36 (3H, s, CH_3), 2.93 (3H, s, CH_3), 6.75 (1H, s, Ar), 7.22-7.34 (1H, d, $j=8.2$, Ar), 8.57 (1H, s, Ar), 8.66 (1H, s, Ar), 8.98 (1H, dd, $J=8.2$, 1.9 Hz, Ar), 9.03 (1H, s, Ar), 9.25 (1H, s, Ar), 10.46 (1H, s, OH); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 24 (2C, CH_3); 39.37 (1C, CH_3); 53.64 (1C); 145.8 (3C, Ar); 149.1 (2C, Ar); 151.37 (4C, Ar); 155.4 (3C, Ar); 161.37 (1C, C-OH); LC-MS, m/z (Irel, %): Found 279.1372 [M+1] (100%), Calculated m/z : 279.2391.

1-((2,3,3-trimethyl-3H-indol-5-yl)diazenyl)naphthalen-2-ol (8b): IR spectrum, wavenumber, cm^{-1} : 3226 (OH-stretch), 2975, 2860 (methyl C-H asym/sym. stretch), 1616-1497 (open-chain azo (-N=N-)), 1382 (aromatic tertiary amine CN stretch), 3030 (C-H aromatic ring stretch); ^1H NMR (400 MHz, CDCl_3 , δ ppm): 1.36 (6H, s, CH_3), 2.27 (3H, s, CH_3), 7.09 (1H, t, Ar), 7.29 (2H, m, Ar), 7.49 (1H, m, Ar), 7.64 (1H, m, Ar), 7.88 (1H, m, Ar), 8.04 (2H, m, Ar), 8.73 (2H, d,

$j=8.4$ Hz, Ar), 9.76 (1H, s, OH); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 12.9 (1C, CH_3); 24.46 (2C, CH_3); 44.5 (1C) 109 (2 C, Ar); 111.47 (2C, Ar); 114.7 (2C, Ar); 124.9 (2C, Ar); 125.17 (2C, Ar), 136.7 (2C, Ar), 142.5 (1C, Ar); 144.2 (2C, Ar), 150 (1C, Ar), 181.03(1C, C-OH); LC-MS, m/z (Irel, %): Found 329.4272 [M+1] (100%), Calculated m/z : 329.1528.

General Experimental Procedure of Diazotization (6, 8c,d) method B:

A mixture of 1 g (5.74 mmol) of 2,3,3-trimethyl-3H-indolenine-5-amine (**5**) in 2.3 mL of 32% HCl and 2.3 mL of water were placed in a 100 mL beaker equipped with a magnetic stirrer. The clear solution was drowned in an ice bath and diazotized with 0.349 g (5.74 mmol) of sodium nitrite dissolved in 1.43 mL of water at 273-282 K. To the clear diazo solution 0.91 g (0.92 mL, 5.74 mmol) of 2,3,3-trimethyl-3H-indolenine (**3**) in 1 mL HCl and 3.2 mL of water were added in small portions under stirring and cooling. After finishing the reaction, 2.6 g (30 mmol) of sodium acetate in 11 mL of water were added. The formed precipitate was filtered, washed with water, and recrystallized from alcohol. 1,2-bis(2,3,3-trimethyl-3H-indol-5-yl)-diazene (**6**) was obtained as a red powder.

N,N-diethyl-4-((2,3,3-trimethyl-3H-indol-5-yl)diazenyl)aniline (8c): IR spectrum, wavenumber, cm^{-1} : 3050 (C-H aromatic ring stretch), 2968, 2926 (methyl C-H asym/sym. stretch), 1594-1512 (open-chain azo (-N=N-)), 1390, 1349 (aromatic tertiary amine CN stretch); ^1H NMR (400 MHz, CDCl_3 , δ ppm): 1.12 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.43 (3H, s, CH_3), 7.05(1H, d, $j=8.6$ Hz, Ar), 8.09 (1H, d, $J=2.3$ Hz, Ar), 8.15 (1H, dd, $j=8.7$, 2.3 Hz, Ar); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 12.9 (1C, CH_3); 24.46 (2C, CH_3); 44.5 (1C) 109 (2C, Ar); 111.47 (2C, Ar); 114.7 (2C, Ar); 124.9 (2C, Ar); 125.17 (2C, Ar), 136.7 (2C, Ar), 142.5 (1C, Ar); 144.2 (2C, Ar), 150 (1C, Ar), 181.03 (1C, C-OH);

4-((2,3,3-trimethyl-3H-indol-5-yl)diazenyl)aniline (8d): IR spectrum, wavenumber, cm^{-1} : 3366, 3214, 3116, (NH_2 stretch), 3031 (C-H aromatic ring stretch), 2963, 2925, 2861 (methyl C-H asym/sym. stretch), 1599-1457 (open-chain azo (-N=N-), 1400, 1309 (aromatic tertiary amine CN stretch), ^1H NMR (400 MHz, CDCl_3 , δ ppm): 0.9 (6H, s, CH_3), 2.07 (3H, s, CH_3), 5.17 (2H, s, NH_2), 7.52-7.54 (2H, d, $j=8.6$ Hz, Ar), 7.71 (2H, d, $J=2.3$ Hz, Ar), 7.93 (1H, m, Ar); 8.13 (1H, s, Ar), 8.44 (1H, s, Ar); ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 28.07 (1C, CH_3); 28.17 (1C, CH_3); 36.5 (1C), 44.9 (1C), 112.1 (1 C, Ar); 116.5 (1C, Ar); 124.6 (1C, Ar); 125.9 (1C, Ar); 127.1 (1C, Ar), 127.4 (1C, Ar), 127.6 (1C, Ar), 128.8 (2C, Ar), 140.5 (1C, Ar), 143.7 (2C, Ar); 177.1 (1C); LC-MS, m/z (Irel, %): Found 279.1659 [M+1] (100%), Calculated m/z 278.1531.

2.2. Methods

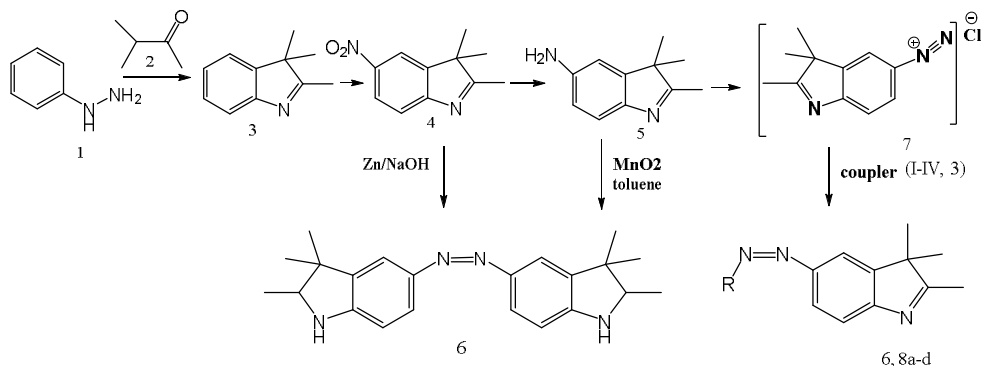
Fourier transform infrared spectra (FTIR) were recorded at Nicolet TM iS50 FTIR Spectrometer-Thermo Fisher Scientific, the infrared region $4000\text{--}400\text{ cm}^{-1}$ (scan 32, resolution 4 cm^{-1}); UV spectra were recorded on GENESYS 50 spectrophotometer Thermo Fisher Scientific.

^1H and ^{13}C NMR spectra were recorded on Bruker NMR-400 (400 MHz) in DMSO-d_6 , or CDCl_3 , with TMS as the internal standard. Mass spectra were recorded on Agilent Technologies 6539 Accurate –Mass Q-TOF LC/MS. Monitoring of the reaction progress and assessment of the purity of synthesized compounds were done by TLC (thin layer chromatography) on Silica gel on TLC PET-foils plates in Hexane/Ethyl acetate, 2:1 eluent system, visualization in an iodine chamber, and UV-light.

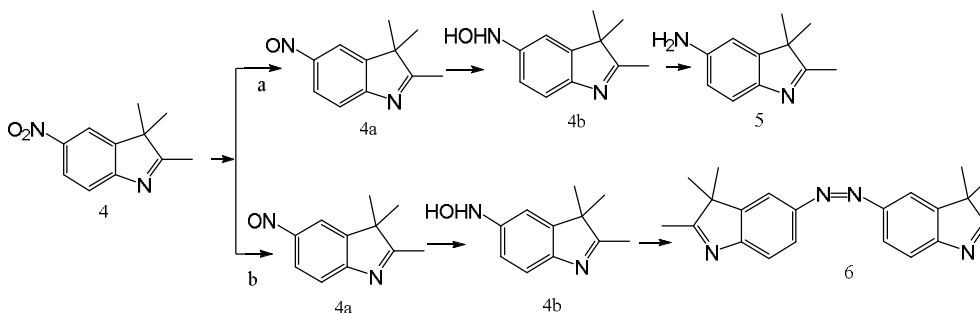
Melting points were determined on a Stuart SM10G (melting temperatures of synthesized azo compounds were determined). It was found that they change color during the heating process, in particular, they darken, decrease in volume, and then turn black. Therefore, melting temperatures are not specified.

3. Results and Discussion

The synthesis of azo compounds was conducted according to Scheme 2. The initial compound (**3**) was



Scheme 2. Synthesis pathway of bis-azo and azo compounds

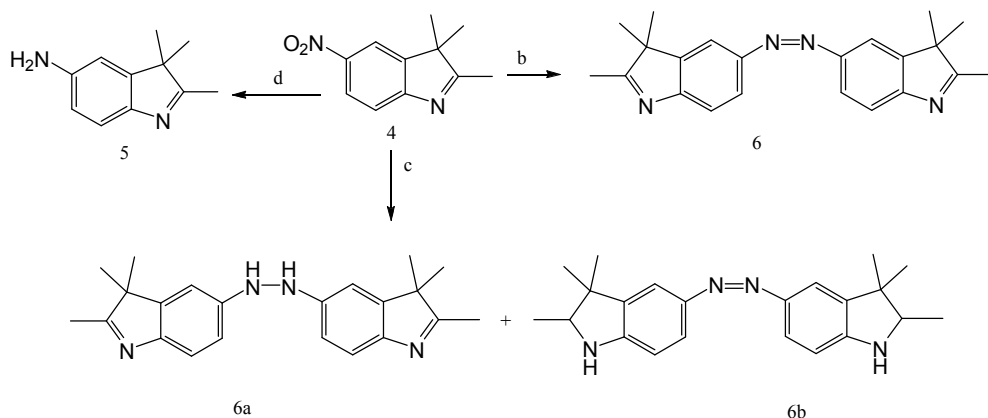


Scheme 3. The reduction of 2,3,3-trimethyl-5-nitro-3H-indolenine: (a) reduction with $\text{Fe}/\text{CH}_3\text{COOH}$ and (b) reduction with Zn/NaOH

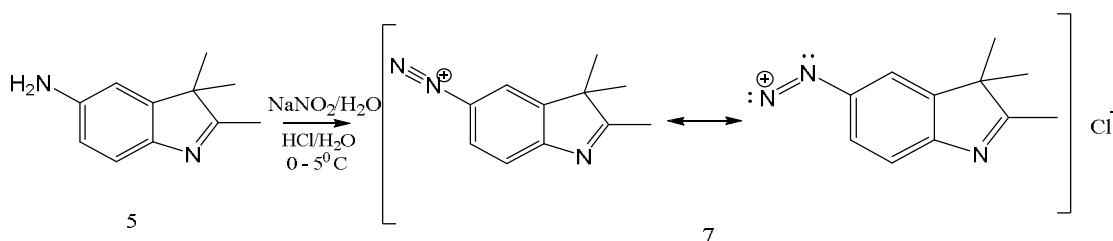
synthesized by a one-step reaction. The condensation reaction of phenylhydrazine (**1**) with methyl isopropyl ketone (**2**) was conducted in the acidic area and 2,3,3-trimethyl-3H-indolenine (**3**) was obtained as a yellowish oil.³¹ Nitration of compound (**3**) with nitration agent at a molar ratio of 1:1:4 (compound 3: $\text{HNO}_3 / \text{H}_2\text{SO}_4$) was carried out and product (**4**) was obtained with a yield of 85%.³²

The reduction of nitro compound (**4**) was studied in two ways, namely, by using easily oxidized metal in the acidic environment³³ ($\text{Fe}/\text{CH}_3\text{COOH}$) (**a**) and by using freshly activated zinc dust in the alkaline solution³⁴ (**b**) (Scheme 3).

Observation of the experiments showed that in the acidic environment (**a**) the first nitroso compound (**4a**) as an intermediate was formed, which was finally reduced to 2,3,3-trimethyl-3H-indolenine-5-amine (**5**) with a 65 % yield. By using freshly activated Zn dust in the alkaline solution (**b**), as an intermediate, nitroso compound (**4a**) was first formed, which was transferred to hydroxylamine (**4b**), and finally, a bis azo (**6**) was formed (Scheme 3). The yield of the obtained azo compound (**6**) was 76 %. It should be noted that depending on the amount of Zn/NaOH , different compounds (**6**), (**4a**), or (**4b**) can be obtained according to Scheme 4. The use of an excessive amount of Zn/NaOH leads to the formation of amine (**5**), which was experimentally confirmed (Scheme 4).



Scheme 4. Reduction of 2,3,3-trimethyl-5-nitro-3H-indolenine with Zn/NaOH: (b) molar ratio of compound (4) : Zn : NaOH as 1:2:4, (c) molar ratio of compound (4) : Zn : NaOH as 2:5:10, and (d) excessive amount of Zn/NaOH



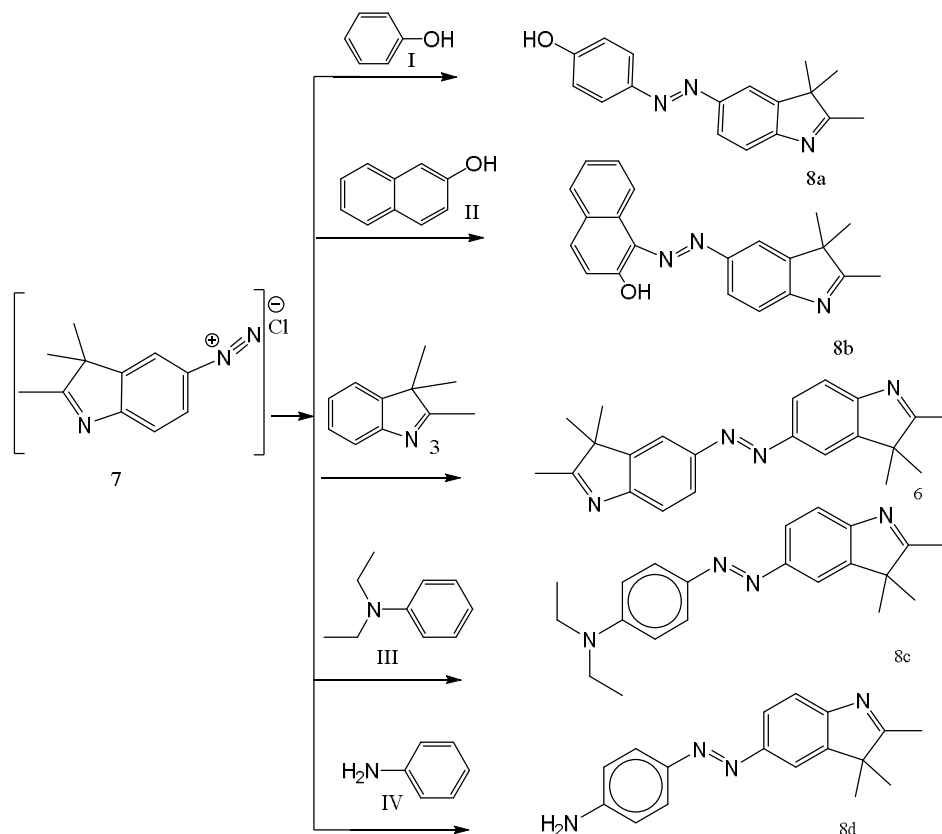
Scheme 5. Synthesis of 2,3,3-trimethyl-3H-indolenine-5-diazonium chloride

The azo dyes with different couplers were synthesized by diazotization of 2,3,3-trimethyl-3H-indolenine-5-amine (5) in an acidic solution, followed by coupling with phenol (I), beta-naphthol (II), 2,3,3-trimethylindolenine (3), N,N-diethylaniline (III), and aniline (IV) according to Schemes 5 and 6. Treatment of nucleophilic 2,3,3-trimethyl-3H-indolenine-5-amine (5) with the electrophilic nitrosonium cation nitrosates the nitrogen of amine (5) and leads to the formation of diazonium salt (7). The temperature of the reaction mixture was kept below 273–282 K. Diazonium salt (7) can be represented by the following two electronic structures, in which the positive charge is shared by both nitrogen atoms.²³⁻²⁵

A coupling of diazonium salt (7) with phenol (I) and beta-naphthol (II) was implemented in the pH range of 8–10. Since diazonium salts are weak electrophiles, they react with phenol (I) and beta-naphthol (II), which were activated by strong electron-donating groups. As a result, C-coupling was formed with the mentioned compound, and corresponding azo dyes (8a) and (8b) were obtained. By coupling compound (7) with 2,3,3-trimethylindolenine (3), N,N-diethylaniline (III), and aniline (IV) in a slightly acidic medium, compounds (6), (8c), and (8d) were synthesized (Scheme 6).

As we mentioned above, the synthesis of bis azo compound (6) was implemented in three different ways

according to Scheme 2. Initially, it was conducted by heating 2,3,3-trimethyl-5-nitro-3H-indolenine (4) in the presence of Zn dust with NaOH in the methanol area, where the molar ratio of the reacting components was 1:2.2:3 (nitro compound (4) : Zn : NaOH). The reaction proceeds very quickly, the red color of the reaction mixture already indicates the formation of a bis azo compound (6). It is desirable to remove the excess catalyst from the reaction mixture immediately after the reaction finishes. The yield of the bis azo compound (6) by the mentioned method was 76%. Bis-azo synthesis was also conducted by oxidation of amine (5). It has been experimentally proven that manganese dioxide as an oxidizing catalyst is actively used in the oxidation of organic compounds. It is quite an effective catalyst for the oxidation of amines, where neutral solvents are often used as the reaction medium.³⁵ In our case, the reaction was carried out by heating 2,3,3-trimethyl-3H-indolenine-5-amine (5) with MnO₂ in toluene, where the molar ratio between the reacting components was 1:5 (amine (5) : MnO₂). The reaction was continued at heating for 15 hours, and the yield of the obtained bis azo compound (6) was 32%. Furthermore, bis azo compound (6) was obtained with the yield of 67% by the method described above, namely, by coupling diazo salt (7) with 2,3,3-trimethylindolenine (3) in an acidic environment.



Scheme 6. Synthesis of azo compounds from 2,3,3-trimethyl-3H-indole-5-diazonium chloride (7)

3.1. FT-IR, ^1H NMR, and ^{13}C NMR Spectra

The structure of the synthesized compounds (3)-(6) and (8a-d) was proved by IR and NMR spectroscopy and mass spectrometry. The IR spectra of compounds (3)-(6) and (8a-d) manifest the characteristic absorption bands of the aromatic ring at 3093-3022 and 1630-1599 cm^{-1} . The

absorption bands of C=N groups in the aromatic ring are observed in their characteristic regions of the spectrum at 1385-1310 cm^{-1} , respectively. The absorption bands of C-NO₂ and NH₂ for compounds (4) and (5) are observed at 1334, 1514, and 3317, 3188 cm^{-1} , respectively. -N=N- groups absorption of compounds (6), (8a-d) appeared at 1616-1473 cm^{-1} .

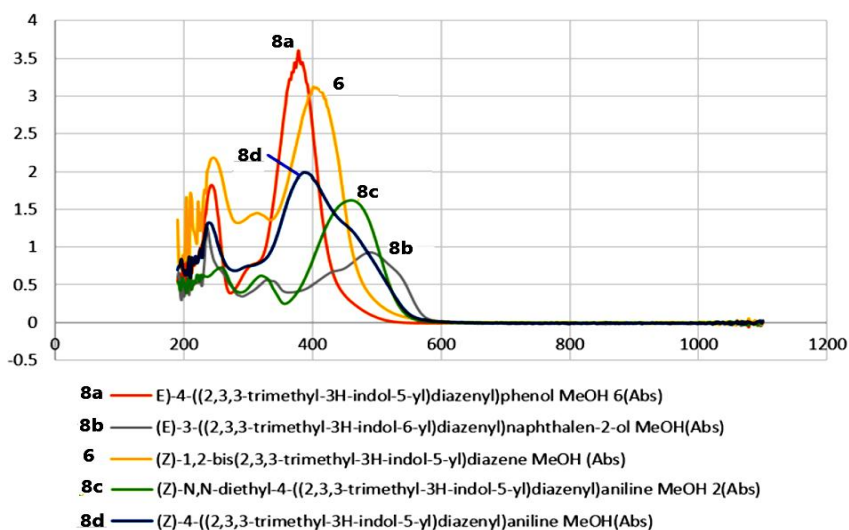


Fig.1. Ultraviolet spectrum of synthesized azo compounds (6a-e)

Table 1. The yield, color, and UV spectrum of compounds (**6**) and (**8a-d**)

Compound	Color	Yield, %	UV spectrum, λ_{max} , nm (log ϵ) [#]
8a	yellow	85	302 (3.383)
8b	milky	65	296 (2.704), 238 (1.23)
6	dark orange	81	378 (3.601), 234 (1.715)
6 (Zn/NaOH)	dark orange	76	
6 (MnO ₂ /toluene)	dark orange	32	
8c	red	78	460 (1.622), 266 (0.754)
8d	reddish	74	392 (1.975), 238 (1.327)

[#] compounds (**6**) and (**8a-d**) were registered in MeOH

The ultraviolet spectrum (Fig. 1) of synthesized azo compounds was studied in methanol. The characteristic absorptions of the azo groups appear at 378 nm to 494 nm. These observations confirm that the aromatic systems on either side of the azo bond between the π and n electrons are conjugated and the given absorption band is due to the azo group. In the case of compound (**8b**), where we have a conjugated system of 2,3,3-trimethyl-3H-indolenine (**3**) with 2-naphthol and -N=N- azo group, the absorption maximum occurs at 494 nm, whereas for compound (**8a**), containing phenol ring, the absorption maximum occurs at 378 nm. The absorption maxima for (**6**), (**8c**), and (**8d**) appear in the range of 392-460 nm (Table 1).

In ¹H NMR spectra of synthesized compounds (**4**)-(b) and (**8a-d**), aromatic proton signals appear as singlets, doublets, doublets of doublets, and multiplets depending on the influence of the respective substituents in the 8.96-6.95 ppm range. NH₂ group signals appear as singlets at 5.16 and 4.97 ppm (compounds (**3**) and (**6e**)). Proton signals of the CH₃ group in the spectra of compounds (**4**)-(b) and (**8a-d**) appear as multiples in the high field region of the spectra. Proton signals of the OH group of compounds (**8a**) and (**6b**) appear as singlet signals at 10.31 and 9.76 ppm.

In ¹³C NMR spectra of compounds (**4**)-(b) and (**8a-d**), the carbon atom signals of the CH₃ group appear in the 16.1-39.37 ppm high field region. Resonance signals of functional groups C=N appear in the 40.0-54.79 ppm regions. The carbon atom signals of the C-OH appear in the 161.37-181.03 ppm regions, respectively. Resonance signals of the aromatic ring appear in the 109-165 ppm regions, respectively.

4. Conclusions

Synthesis of azo compounds based on 2,3,3-trimethyl-3H-indolenine was conducted by the reduction of the nitro compound using Zn dust in the presence of NaOH aqueous solution; by heating of 2,3,3-trimethyl-3H-indolenine-5-amine in toluene in the presence of MnO₂; and by diazotization of 2,3,3-trimethyl-3H-

indolenine-5-amine and its interaction with the appropriate couplers it was experimentally proven that azo compounds were obtained in a relatively good yield by diazotization of amine and its subsequent interaction with couplers. By reducing the nitro compound using Zn/NaOH, it was possible to obtain bis azo with a higher yield, compared with heating the amine in toluene using a MnO₂ catalyst. The structures were determined by IR, NMR, and mass spectral analyses, which were consistent with the structures of the synthesized compounds.

References

- [1] Benkhaya, S.; Harfi, A. E.; El Harfi, A. Classifications, Properties and Applications of Textile Dyes: A Review. *Appl. J. Environ. Sci.* **2017**, *3*, 311-320. <https://doi.org/10.48422/IMIST.PRSM/ajeess-v3i3.9681>
- [2] Mikroyannidis, J.A.; Tsagkournos, D.V.; Balraju, P.; Sharma G.D. Low Band Gap Dyes Based 3 on 2-Styryl-5-phenylazopyrrole: Synthesis and Application for Efficient Dye-Sensitized Solar Cells. *J. Power Sources* **2011**, *196*, 4152-4161. <https://doi.org/10.1016/j.jpowsour.2010.12.038>
- [3] Al-Ahmad, A.Y.; Hassan, Q.M.A.; Badran, H.A.; Hussain, K.A. Investigating Some Linear and Nonlinear Optical Properties of the Azo Dye (1-Amino-2-hydroxy naphthalin sulfonic acid-[3-7(4-azo)]-4-amino diphenyl sulfone). *Opt. Laser Technol.* **2012**, *44*, 1450-1455. <https://doi.org/10.1016/j.optlastec.2011.12.019>
- [4] Pevzner, E.; Ehrenberg, B. Principal Component Analysis of the Absorption and Resonance Raman Spectra of the Metallochromic Indicator Antipyrilazo III. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2000**, *56*, 637-651. [https://doi.org/10.1016/S1386-1425\(99\)00164-X](https://doi.org/10.1016/S1386-1425(99)00164-X)
- [5] Feng, Y.; Liu, H.; Luo, W.; Liu, E.; Zhao, N.; Yoshino, K.; Feng, W. Covalent Functionalization of Graphene by Azobenzene with Molecular Hydrogen Bonds for Long-Term Solar Thermal Storage. *Sci. Rep.* **2013**, *3*, 3260. <https://doi.org/10.1038/srep03260>
- [6] Adegoke, O.A.; Adesuji, T.E.; Thomas, O.E. Novel Colorimetric Sensors for Cyanide Based on Azo-Hydrazone Tautomeric Skeletons. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2014**, *128*, 147-152. <https://doi.org/10.1016/j.saa.2014.02.118>
- [7] Coelho, P.J.; Carvalho, L.M.; Fonseca, A.M.C.; Raposo, M.M.M. Photochromic Properties of Thiénylpyrrole Azo in Solution. *Tetrahedron Lett.* **2006**, *47*, 3711-3714. <https://doi.org/10.1016/j.tetlet.2006.03.125>
- [8] Ruyffelaere, F.; Nardello, V.; Schmidt, R.; Aubry, J.M. Photosensitizing Properties and Reactivity of Aryl Azo Naphthol Dyes

- Towards Singlet Oxygen. *J. Photochem. Photobiol.* **2006**, *183*, 98-105. <https://doi.org/10.1016/j.jphotochem.2006.02.029>
- [9] Erfantalab, M.; Khanmohammadi, H. New 1,2,4-Triazole-Based Azo–Azomethine Dye. Part III: Synthesis, Characterization, Thermal Property, Spectrophotometric and Computational Studies. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2014**, *125*, 345-352. <https://doi.org/10.1016/j.saa.2014.01.113>
- [10] Sabet, R.A.; Khoshsim, H. Real-Time Holographic Investigation of Azo Dye Diffusion in a Nematic Liquid Crystal Host. *Dyes Pigm.* **2010**, *87*, 95-99. <https://doi.org/10.1016/j.dyepig.2010.02.009>
- [11] Kim, Y.D.; Cho, J.H.; Park, C.R.; Choi, J.H.; Yoon, C.; Kim, J.P. Synthesis, Application and Investigation of Structure–Thermal Stability Relationships of Thermally Stable Water-Soluble azo Naphthalene Dyes for LCD Red Color Filters. *Dyes Pigm.* **2011**, *89*, 1-8. <https://doi.org/10.1016/j.dyepig.2010.07.008>
- [12] Avella-Oliver, M.; Morais, S.; Puchades, R.; Maquieira, A. Towards Photochromic and Thermochromic Biosensing. *Trends Analyt. Chem.* **2016**, *79*, 37-45. <https://doi.org/10.1016/j.trac.2015.11.021>
- [13] Zhang, X.; Hou, L.; Samori, P. Coupling Carbon Nanomaterials with photochromic Molecules for the Generation of Optically Responsive Materials. *Nat. Commun.* **2016**, *7*, 11118. <https://doi.org/10.1038/ncomms11118>
- [14] Benkhaya, S.; Mrabet, S.; El Harfi, A. Classifications, Properties, Recent Synthesis and Applications of Azo Dyes. *Heliyon* **2020**, *6*, 03271. <https://doi.org/10.1016/j.heliyon.2020.e03271>
- [15] Esser-Kahn, A.P.; Odom, S.A.; Sottos, N.R.; White, S.R.; Moore, J.S. Triggered Release from Polymer Capsules. *Macromolecules* **2011**, *44*, 5539-5553. <https://doi.org/10.1021/ma201014n>
- [16] Yousefi, H.; Yahyazadeh, A.; Moradi Rofchahi, E.O.; Rassa, M. Synthesis, Spectral Properties, Biological Activity and Application of new 4-(Benzyloxy)phenol Derived Azo Dyes for Polyester Fiber Dyeing. *J. Mol. Liq.* **2013**, *180*, 51-58. <https://doi.org/10.1016/j.molliq.2012.12.030>
- [17] Mallikarjuna, N.M.; Keshavayya, J. Synthesis, Spectroscopic Characterization and Pharmacological Studies on Novel Sulfamethazole Based Azo Dyes. *J. King Saud Univ. Sci.* **2020**, *32*, 251-259. <https://doi.org/10.1016/j.jksus.2018.04.033>
- [18] Yazdanbakhsh, M.R.; Yousefi, H.; Mamaghani, M.; Moradi, E.O.; Rassa, M.; Pouramir, H.; Bagheri, M. Synthesis, Spectral Characterization and Antimicrobial Activity of Some New Azo 3 Dyes Derived from 4,6-Dihydroxypyrimidine. *J. Mol. Liq.* **2012**, *169*, 21-26. <https://doi.org/10.1016/j.molliq.2012.03.003>
- [19] Karci, F.; Şener, N.; Yamaç, M.; Şener, İ.; Demirçali, A.A. The Synthesis, Antimicrobial Activity and Absorption Characteristics of Some Novel Heterocyclic Disazo Dyes. *Dyes Pigm.* **2009**, *80*, 47-52. <https://doi.org/10.1016/j.dyepig.2008.05.001>
- [20] Xu, H.; Zeng, X. Synthesis of Diaryl-Azo Derivatives as Potential Antifungal Agents. *Bioorgan. Med. Chem. Lett.* **2010**, *20*, 4193-4195. <https://doi.org/10.1016/j.bmcl.2010.05.048>
- [21] Liu, G.; Wang, X.; Hu, J.; Zhang, G.; Liu, S. Self-Immolative Polymersomes for High-Efficiency Triggered Release and Programmed Enzymatic Reactions. *J. Am. Chem. Soc.* **2014**, *136*, 7492-7497. <https://doi.org/10.1021/ja5030832>
- [22] Mohamed-Smati, S.B.; Faraj, F.L.; Becheher, I.; Berredjem, H.; Bideau, F.L.; Hamdi, M.; Dumas, F.; Rachedi, Y. Synthesis, Characterization and Antimicrobial Activity of Some New Azo Dyes Derived from 4-Hydroxy-6-methyl-2H-pyran-2-one and its Dihydro Derivative. *Dyes Pigm.* **2021**, *188*, 109073. <https://doi.org/10.1016/j.dyepig.2020.109073>
- [23] Hunger, K.; Mischke, P. Azo Dyes, 1. *Ullmann's encycl. ind. chem.* **2011**, *4*, 523-541. https://doi.org/10.1002/14356007.a03_245.pub2
- [24] Hunger, K.; Mischke, P.; Rieper, W.; Raue, R.; Kunde, K.; Aloys E. Azo Dyes. *Ullmann's encycl. ind. chem.* **2000**, 1-93. https://doi.org/10.1002/14356007.a03_245
- [25] Gung, B.W.; Taylor, R.T. Parallel Combinatorial Synthesis of Azo Dyes: A Combinatorial Experiment Suitable for Undergraduate Laboratories. *J. Chem. Educ.* **2004**, *81*, 1630-1632. <https://doi.org/10.1021/ed081p1630>
- [26] Rydchuk, M.; Vrublevska T.; Boyko M.; Korkuna, O. Masking is the Effective Alternative to the Separation during Osmium Determination by Means of Azo Dyes in Complex Samples. *Chem. Chem. Technol.* **2010**, *4*, 115-124. <https://doi.org/10.23939/chcht04.02.115>
- [27] Nadtoka, O. Nonlinear Optical Effects in Polymeric Azoesters. *Chem. Chem. Technol.* **2010**, *4*, 185-190. <https://doi.org/10.23939/chcht04.03.185>
- [28] Naji, A.M.; Abdula, A.M.; Nief O.A.; Abdullah, E.K. Synthesis, Characterization, Antimicrobial and Molecular Docking Study of Benzooxadiazole Derivatives. *Chem. Chem. Technol.* **2022**, *16*, 25-33. <https://doi.org/10.23939/chcht16.01.025>
- [29] Kulkarni, M.; Thakur, P. The Effect of UV/TiO₂/H₂O₂ Process and Influence of Operational Parameters on Photocatalytic Degradation of Azo Dye in Aqueous TiO₂ Suspension. *Chem. Chem. Technol.* **2010**, *4*, 265-270. <https://doi.org/10.23939/chcht04.04.265>
- [30] Gilbert, A.M.; Failli, A.; Shumsky, J.; Yang, Y.; Severin, A.; Singh, G.; Hu, W.; Keeney, D.; Petersen, P.J.; Katz, A.H. Pyrazolidine-3,5-diones and 5-Hydroxy-1H-pyrazol-3(2H)-ones, Inhibitors of UDP-N-acetylenolpyruvyl Glucosamine Reductase. *J. Med. Chem.* **2006**, *49*, 6027-6036. <https://doi.org/10.1021/jm060499t>
- [31] Hugo, I.; Funderburk, L.H. Process for the Preparation of 2,3,3-Trimethyl Indolenines, US3639420 A, February 1, 1972.
- [32] Piggott, H.A.; Hulme, Ch. Heterocyclic Nitrogen Compounds. US2016836, October 8, 1935.
- [33] Lyubich, M.S.; Isaev, S.G.; Al'perovich, M.A.; Shpileva, I.S.; Arshava, B.M. Interaction of 5-Amino-2,3-trimethyl-3H-indole with p-Nitrobenzaldehyde. *Chem. Heterocycl. Compd.* **1984**, *20*, 976-977. <https://doi.org/10.1007/BF00506391>
- [34] Bigelow, H.E.; Robinson, D.B. Azobenzene. *Org. Synth.* **1942**, *22*, 103. <https://doi.org/10.15227/orgsyn.022.0028>
- [35] Bhatnagar, I.; George M.V. Oxidation of Phenylhydrazones with Manganese Dioxide. *J. Org. Chem.* **1967**, *32*, 2252-2256. <https://doi.org/10.1021/jo01282a036>

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СИНТЕЗ ДЕЯКИХ АЗОБАРВНИКІВ НА ОСНОВІ 2,3,3-ТРИМЕТИЛ-3Н-ІНДОЛЕНІНУ

Анотація. Нові азосполуки на основі 2,3,3-триметил-3Н-індоленіну синтезовано й охарактеризовано за допомогою ІЧ-, ЯМР- і мас-спектрального аналізу. Синтез проводили трьома різними маршрутами: 1) відновленням нітросполуки за допомогою Zn/NaOH у спирті; 2) нагріванням 2,3,3-триметил-3Н-індоленін-5-аміну в присутності MnO₂ в толуолі; 3) діазотуванням 2,3,3-триметил-3Н-індоленін-5-аміну й обробкою отриманої солі діазонію відповідною азоскладовою.

Ключові слова: азобарвники, біс-азобарвник, відновлення, 2,3,3-триметил-3Н-індоленін, синтез.