NAPHTOINDOLE ECOLOGICAMENTE CORRETO CONTENDO CORANTES AZO

ENVIRONMENTALLY FRIENDLY NAPHTOINDOLE CONTAINING AZO DYES

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Received 3 February 2014; received in revised form 8 February 2014; accepted 12 February 2014

RESUMO

No presente trabalho são discutidos caminhos para a síntese de alguns corantes azo a partir de compostos aromáticos menos ativos, incluindo os biologicamente ativos. Os compostos naphtho[1,2-g]indole e naphtho[2,1-g]índole contendo corantes azo foram sintetizados em um meio orgânico não-polar através de catálise de transferência de fase. Os corantes obtidos são adequados para conferir cor ao nylon e fibras de poliéster de amarelo claro ao vermelho com alto grau de qualidade. O corantes azo resultantes podem ser caracterizados como compostos menos tóxicos devido a regentes metabólicos não-tóxicos. Ainda, cálculos químico-quânticos foram processados com o auxílio dos métodos de mecânica quântica (MM2) e semi-empírico (AM1), que permitem predizer a atividade dos corantes em relação ao ligante AhR.

Palavras-chave: corantes azo, acoplamento, heterocíclicos, catálise de transferência de fase

ABSTRACT

In the present article there are discussed the ways of synthesis of some azo-dyes from less active aromatic compounds, including biologically active ones. The novel naphtho[1,2-g]indole and naphtho[2,1-g]indole containing azo dyes have been synthesized in the non-polar organic media under phase transfer catalysis. Obtained disperse dyes are suitable for dyeing nylon and polyester fibers from light yellow to red color with good-excellence dyeing levelness, light, washing and sublimation fastness. The resulting azo dyes may be characterized as the less toxic compounds due to non-toxic metabolism reagents. Additionally, the quantum-chemical calculations have been performed using quantum mechanical (MM2) and semi-empirical (AM1) methods, which allow to predict the activity of dyes against AhR ligand.

Keywords: *Azo Dyes, Coupling, Heterocycles, Phase Transfer Catalysis*

INTRODUCTION

Azo dyes are used in a variety of industries, including textile, cosmetics, food, leather and paper industries. However, some azo compounds manifest carcinogenicity due to the high reactivity of their metabolic intermediates and can react covalently with DNA and cause mutations (Ferraz, E. R.A.;Grando, M. D.; Oliveira, D. P. 2011; Smetanina, M. A.; Pakharukova, M. Y.;Kurinna, S. M.; Dong, B.; Hernandez, J. P.; Moore, D. D.;Merkulova, T. 2011; Srinivasan, K.; Bhargava, M.M. 2004).

The one possible way to avoid formation of such reactive carcinogenic metabolic compounds is the construction of azo dyes from biologically active or non-toxic azo and diazo partners. But most biologically active compounds are unable to react to diazonium salts due to their decreased reaction ability in azo coupling

DOI: 10.52571/PTQ.v11.n20-21.2013.47_Periodico20e21_pgs_47_53.pdf

reaction under classical conditions (water or polar organic media, 0-5°C). For example many indole containing compounds exhibit reach biologically active properties, although they are very weak azo partners. Nanaphto[1,2-g]-indole and naphto[2,1-g]indole were proposed to have a tubercular static activity (Razmadze, T.; Legashvili, I.; Shubitidze, A.; Kereselidze, J.; Buyanov, V.; Chirakadze, G. 2002; Razmadze, T.;Buyanov, V; Chirakadze, G.;Elizbarashvili, E. 2005).

On the other hand some halogenated azo compounds (i.e. 2',6'-dichloro-4-dimethylaminoazobenzene and others) have the greatest enhancement of the AhR ligand activity and are a good receptors of dioxin (Gonzalez, F-J.; Fernandez-Salguero, P. 1998; Chou, PH.; Matsui, S.;Matsuda. T. 2006).

Here we report the synthesis of some new naphtho[1,2-g]indole and naphtho[2,1-g]indolecontaining azo dyes in the non-polar organic media under phase transfer catalysis and investigation of their spectral and physical-chemical characteristics. In addition, the quantum-chemicalcalculations have been performed using quantum mechanical (MM2) and semi-empirical (AM1) methods. These calculations are valuable for providing insight into the structure-activity correlation, and are usefulfor the prediction of the toxicity of some structurally related compounds.

MATERIALS AND METHODS

All of the used chemicals were of commercial grade and were further purified be recrystallization and redistilled before use. The solvents were spectroscopic grade. The IR spectra were obtained on a Thermo Nikolet spectrometer scanning between 4,000-400 cm^{-1} using KBr plates. UV-Vis absorption spectra were measured in CF-26 (produced in Russia). Elemental analysis was performed using Heraeous CHNO-Rapid analyzer. Melting points were determined by Electrothermal 9100.

2.1. *Diazotization of aromatic amines*

Aromatic amines **1a-c** (1 mmol) was dissolved in the tetrafluoroboric acid (48%, 4 mmol) with vigorous stirring in the Teflon beaker at 25°C. The solution of sodium nitrite (1.2 mmol) in water (2 ml) was added dropwise and stirring was continued for additional 2 hours. After finishing diazotization process the excess of HNO_2 was removed by addition of urea. The precipitated white solids was filtered off on the Buchner funnel and washed with cold water, diethyl ether and cold methanol. Obtained crystals were dried between filter papers on the air to affordtetrafluoroborates**2a-c** in 55-58% yield.

2.2. Azo coupling in non-polar media

Naphto[1,2-g]indole (**3**) or naphto[2,1-g]indole (**4**) (0.01 mol) was placed in the 100 ml beaker and dissolved in chloroform (25 ml). Solid tetraflouroborates**2a-c** (0.01 mol) and phase transfer catalysts (dibenzo-18-crown-6, dodecyltrimethylammonium chloride or sodium *p-tert.*-butylbenzenesulphonate) (0.01 mol) were added to the azo partner solution and the reaction mixture was stirred for a period of 48 hours. Obtained colored solution was filtered and evaporated under reduced pressure. The residue was purified by crystallization from ethanol.

*1-((2,4-dinitrophenyl)diazenyl)-3H-aphtho[1,2-g]indole (**4a**).* Yield 38%, m.p. 180-182°C. Elemental analysis: Calculated for $C_{22}H_{13}N_5O_4$ C, 64.20; H, 3.24; N, 17.05. Found: C, 64.21; H, 3.20; N, 17.12.λ_{max}(nm, lgε, ethanol): 430 (6.45). IR spectrum (cm^{-1}): 3124 (NH), 3000(CH), 1610 (N=N), 1600 C=C), 1575 (NO_2), 1530 (C-H), 1360 (NO_2), 1308 (C-N), 1202 (CH).

*1-((2-chloro-4-nitrophenyl)diazenyl)-3H-naphtho[1,2-g]indole (**4b**).*Yield 35%, m.p. 113-115°C. Elemental analysis: Calculated for $C_{22}H_{13}ClN_4O_2$ C, 65.92; H, 3.27; Cl, 8.85; N, 13.98. Found: C, 65.90; H, 3.22; Cl, 8.81; N, 14.00. λ_{max}(nm, lgε, ethanol): 460 (5.98). IR spectrum (cm^{-1}): 3124 (NH), 3000 (CH), 1613 (N=N), 1600 (C=C), 1575 (NO_2), 1360 (NO_2), 1308 (C-N), 1202 (CH), 650 (C-Cl).

*1-((2-cyano-4-nitrophenyl)diazenyl)-3H-naphtho[1,2-g]indole (**4c**).*Yield 20%, m.p. 179-181°C. Elemental analysis: Calculated for $C_{23}H_{13}N_5O_2$ C, 70.58; H, 3.35; N, 17.89. Found: C, 70.60; H, 3.40; N, 18.00. λ_{max}(nm, lgε, ethanol): 450 (5.25). IR spectrum (cm^{-1}): 3150 (NH), 3060 (CN), 1610 (N=N), 1600 (C=C), 1575 (NO_2), 1345 (NO_2).

*3-((2,4-dinitrophenyl)diazenyl)-1H-naphtho[2,1-g]indole (**5a**).*Yield 35%, m.p. 160-162°C. Elemental analysis: Calculated for $C_{22}H_{13}N_5O_4$ C, 64.20; H, 3.24; N, 17.05. Found: C, 64.35; H,

3.31; N, 17.00.λ_{max}(nm, lgε, ethanol): 440 (6.21). IR spectrum (cm^{-1}): 3125 (NH), 3000(CH), 1610 (N=N), 1600 (C=C), 1570 (NO_2), 1520 (C-H), 1420 (C-H), 1390 (NO_2), 1310 (C-N), 1210 (CH).

*3-((2-chloro-4-nitrophenyl)diazenyl)-1H-naphtho[2,1-g]indole (**5b**).*Yield 37%, m.p. 113-115°C. Elemental analysis: Calculated for $C_{22}H_{13}ClN_4O_2$ C, 65.92; H, 3.27; Cl, 8.85; N, 13.98. Found: C, 65.95; H, 3.20; Cl, 8.90; N, 14.10. λ_{max}(nm, lgε, ethanol): 450 (6.12). IR spectrum (cm^{-1}): 3120(NH), 3030 (CH), 1624 (N=N), 1610 (C=C), 1580 (NO_2), 1370 (NO_2), 1315 (C-N), 1200 (CH), 650 (C-Cl).

*1-((2-cyano-4-nitrophenyl)diazenyl)-1H-naphtho[2,1-g]indole (**5c**).*Yield 24%, m.p. 196-198°C. Elemental analysis: Calculated for $C_{23}H_{13}N_5O_2$ C, 70.58; H, 3.35; N, 17.89. Found: C, 70.66; H, 3.38; N, 17.90. λ_{max}(nm, lgε, ethanol): 465 (5.75). IR spectrum (cm^{-1}): 3155 (NH), 3056 (CN), 1608 (N=N), 1600 (C=C), 1572 (NO_2), 1340 (NO_2).

2.3.Method of Calculation

Initial molecular geometry was optimized using MM+ molecular modeling and semi-empirical AM1 methods (Hyperchem-6.03, Hypercube, Ontario, Canada). In the next step RHF calculation were performed and bond length, angles, torsion angles and partial charges have been calculated.

RESULTS AND DISCUSSION:

3.1 Synthesis

Arendiazonium ions are a weak electrophilic species able to couple only with activated aromatic compounds (azo partners). Naphto[1,2-g]-(**3**) and naphto[2,1-g]indoles (**4**) react to various electrophilic reagents and form 3-substituted derivatives (Razmadze, T.; Buyanov, V.; Chirakadze,G.; Elizbarashvili,E 2005). Although,**3** and **4** are inactive in azo coupling reaction. All our attempts to obtain azo dyes from**3** or **4**in water media were unsuccessful. In our opinion, the reason of experiment failure is the decreased electrophilicity of diazonium cation due to solvatation effect and charge delocalization on β-nitrogen atom of diazo group.

In our previous paper, we declare that some azo partner compounds of low activity may couple with arendiazonium salts in the low polar organic media (*i.e.* chloroform) in the presence of phase transfer catalysts (Elizbarashvili, E.; Baidoshvili, P.;Chirakadze, G. 2000) and form azo dyes. Therefore, we decided to use the aforementioned procedure for the synthesis of desired indole containing dyes. Due to the fact that **3** and **4** do not possess some electron donating groups, strong electron withdrawing group possessing aminobenzenes such as 2,4-dinitroaniline (**1a**), 2-chloro-4-nitroaniline (**1b**) and 2-cyano-4-nitroaniline (**1c**) have been chosen as diazo partners.**1a-c**were diazotized with the mixture of sodium nitrite and tetrafluoroboric acid and formed diazonium tetrafluoroborates**2a-c** were isolated as a stable crystalline solids (Scheme 1). **2a-c**have low solubility in the water and are insoluble in the non-polar organic aprotic solvents (*i.e.* chloroform). For the aim of **2a-c**solubilization in the chloroform dibenzo-18-crown-6(**7**), dodecyltrimethyl ammoniumchloride (**8**) and sodium *p-tert.*-butylbenzenesulphonate(**9**) as a phase transfer catalysts (PTC) were employed.

Table 1. *The yields, color and common properties of dyes 5 and 6*

Dye	Yield, %	PTC	R_f	λ_{max}(log ε)[a]
5a	38	**7**	0.155[b]	430 (6.45)
5a	15	**8**	0.155[b]	430 (6.45)
6a	30	**9**	0.155[b]	430 (6.45)
7b	35	**7**	0.145[c]	460 (5.98)
5c	20	**7**	0.169[c]	450 (5.25)
6a	35	**7**	0.150[b]	440 (6.21)
6b	37	**7**	0.145[c]	450 (6.12)
6b	20	**9**	0.145[c]	450 (6.12)
6c	24	**7**	0.145[c]	465 (5.75)

–Solvent: ethanol, (b)-eluent: toluene - ethyl acetate, 3:1 (v/v), (c)- eluent: benzene - ethyl acetate 3:1 (v/v).

Thepresence of electron-attracting groups (chlorine and nitro) in “diazo partner” at suitable positions (ortho- and para-) in the coupled ring weakly affects the absorption characteristics on the dyes, despite the fact, that dye consist five aromatic rings. This is due to absence of electron-donating groups in “azo partner” (weak push-pull effect).

3.2. Infrared spectra of dyes

The infrared spectra of **5a-c** and **6a-c** contain characteristic bands at 3355-3300 cm^{-1}, which indicate heterocyclic N-H stretching. The strong bands, observed at 1609-1600 cm^{-1} indicates stretching vibration of the C-C aromatic skeleton.
The stretching near 1600 cm^{-1} corresponds to azo group. The bands at 1583-1575 cm^{-1} and 1393-1380 cm^{-1} are due to the nitro groups.

3.3. Kinetic study

Kinetics of the azo coupling reaction were followed under pseudo-first-order conditions (**2a-c** at least tenfold excess) by monitoring the appearance of an absorption band due to the product of azo coupling reaction at 450 nm). Excellent pseudo-first-order kinetic plots covering at least 2 half-lives were obtained. Quantitative yields of azo coupling products were determined by comparison of the absorption at 450 nm in infinity samples with then calculated using the extinction coefficient of an authotentic sample of **5a-c** and **6a-c**. Reaction rate pseudo-first-order constants are in the range of 6.567- 6.680×10^{-6} s^{-1} in chloroform media.

3.4. Dyeing performance of dyes

The disperse azo dyes **5a-c** and **6a-c** were applied at 1.8-2% depth on polyester and nylon fibers. Dyes **5a-c** and **6a-c** gave yellow and red hues with good levelness, brightness and depth on the used fibers. The dyed nylon and polyester showed good-excellence fastness to light, washing, rubbing and perspiration and excellence fastness to sublimation. The insignificant changes of levelness after washing indicate to good dye penetration and affinity to the employed fibers.

3.5. Quantum-chemical calculations

The optimized geometric parameters (bond lengths, bond angles and torsion angles) of **5b** and **6b** by RHF with basic sets of Chem3D are listed in the tables3-5. The atom numbers are shown on models of dye molecules represented on fig.1 and fig.2.

According to these results both molecules have trans-geometry about azo linkage. The optimized structure of **5b** is found to be planar, while **6b** being non-planar. The torsion angles of C4-C5-N7-N8 in **5b** were calculated to be close to 0°, while the torsion angle C27-N19-N20-C20 in **6b** about 50°. Based on this data and the similar trend observed with chlorinated dimethylaminoazobenzene (Yang, W.;You,X-L.;Zhang,Y.;Zhang, D-Ch 2006), we can suggested that non-planarity of the dye **6b** may contribute to the higher AhR ligand activity then the planar structure of the dye **5**.

Distribution of the electronic density in the molecules **5b** and **6b** shows, that the largest negative charge is located on the nitrogen atom of indole moiety. The sufficiently large negative charge value may indicate the activity of the N-H bond, which is important for further transformations (i.e. immobilization) in the molecule. See Table 1; 2; 3 and 4.

Table 2.*Selected bond lengths of optimized geometries of azo dyes 5b and 6b*

Dye 5b		**Dye 6b**	
Cl26-C4	1.6975 Å	Cl29-C27	1.69507 Å
C4-C5	1.4187 Å	C27-C17	1.41396 Å
N7-C5	1.4333 Å	N19-C17	1.43378 Å
N7-N8	1.2382 Å	N19-N20	1.23489 Å
N8-C25	1.3993 Å	N20-C24	1.40107 Å
C24-C25	1.4176 Å	C24-C25	1.41457 Å
C20-C25	1.4557 Å	C24-C13	1.45503 Å

Table 3.*Selected bond angles of optimized geometries of azo dyes 5b and 6b*

Dye 5b		**Dye 6b**	
Cl26-C4-C5	121.6Å	Cl29-C27-C17	121.9Å
C4-C5-N7	116.6Å	C27-C17-N19	124.4Å
C5-N7-N8	119.5Å	C17-N19-N20	119.5Å
N7-N8-C25	118.8Å	N19-N20-C24	119.2Å
N8-C25-C24	130.3Å	N20-C24-C25	130.8Å
N8-C25-C20	123.2Å	N20-C24-C13	122.6Å

Table 4.*Selected bond torsion angles of optimized geometries of azo dyes 5b and 6b*

Dye 5b		**Dye 6b**	
Cl26-C4-N7-N8	0.006°	Cl29-C27-C17-N19	4.876°
C4-C5-N7-N8	0.017°	C27-C17-N19-N20	50.144°
C5-N7-N8-C25	0.050°	C17-N19-N20-C24	0.052°
N7-N8-C25-C24	0.038°	N19-N20-C24-C25	3.202°

CONCLUSIONS:

Introduction of the of phase transfer catalysts into the azo coupling reaction in the non-polar organic solvents helps to improve a solubility of the starting components of the reaction and gives an opportunity to obtain azo dyes from low active aromatic compound, including biological active ones. The resulting azo dyes may be characterized as the less toxic compounds due to non-toxic metabolism reagents.

ACKNOWLEDGMENTS:

The authors thank Prof. Sh. Samsoniyaand Prof. J. Kereselidzefrom Javakhishvili Tbilisi State University for providing valuable advices in chemistry of nathoindoles and quantum-chemical calculations.

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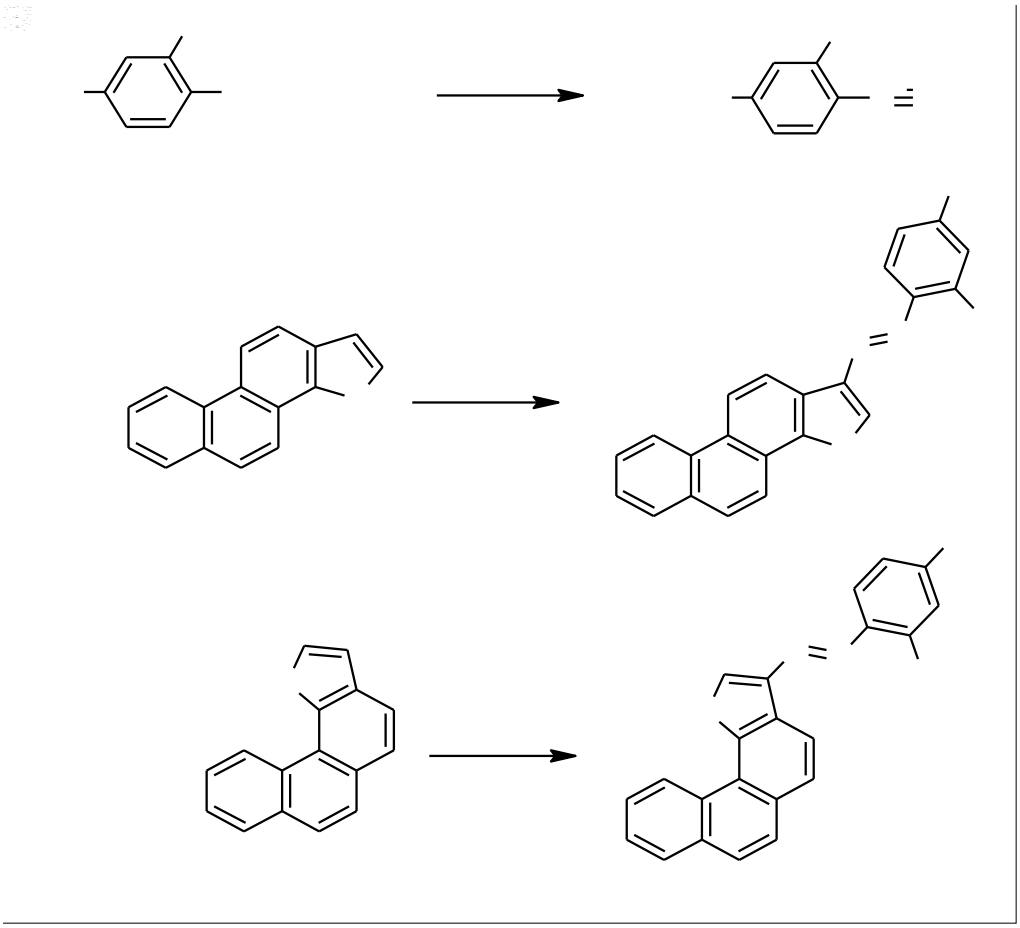

Scheme 1. Synthesis of azo dyes. a: R_1=NO_2,R_2=NO_2; b:Cl, R_2=NO_2; c: R_1=CN, R_2=NO_2; PTC is either dibenzo-18-crown-6, dodecyltrimethylammonium chloride or sodium *p-tert.*-butylbenzenesulphonate

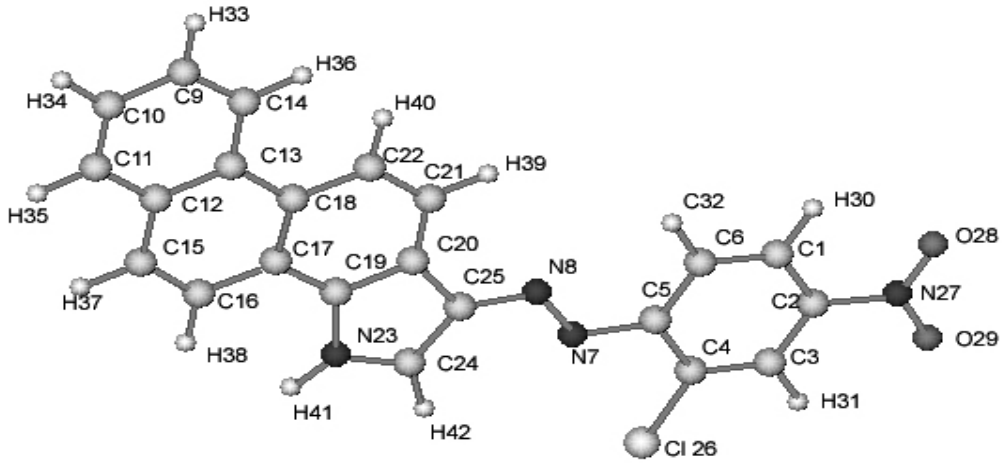

Figure 1. Optimized molecular structure of dye 5b

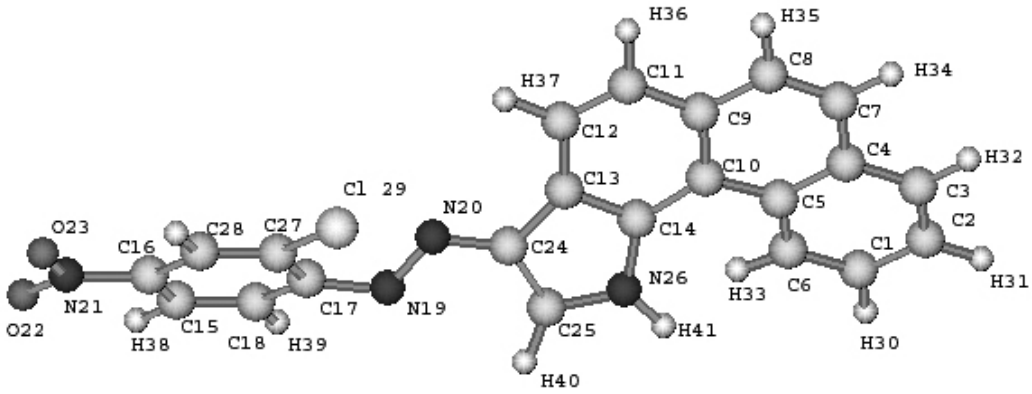

Figure 2. Optimized molecular structure of dye 6b