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Synthesis of Some Novel Derivatives of 2,6-Diaminoanthraquinone Dyes

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In present study, some derivatives of 2,6-diaminoanthraquinone dyes are synthesized and their UV-visible spectra are investigated in various conditions. Ten compounds (**1a-e**) and (**2a-e**), two of which (**1a, 1b**) were previously obtained in low yields, have been synthesized by using diazonium salts of 2,6-diaminoanthraquinone and characterized by spectroscopic methods.

Key Words: 2,6-Diaminoanthraquinone, Anthraquinone dyes, Liquid crystal dyes.

INTRODUCTION

Anthraquinone dyes are an important class of dyes[1] and quinones today[2] although, till 1970 they were only considered as the types available for dyeing polyester to brilliant in blues. In recent years, many studies dealing with synthesis and acid base, electrochemical, pharmacological, photochemical and photophysical properties of these dyes appeared in the literature[2-5].

One of the most important uses of anthraquinone dyes is guest-host (GH) display systems used as liquid crystal dyes. The performance of guest-host type liquid crystal display (LCD) is in conjunction with the solubility and dissolution stability of dichroic dyes[6,7]. In GH-LCDs, a small amount of dye (guest) is dissolved in a liquid crystalline media (host) which acting as a substance to orient the guest molecules. When electric field is applied to the display, the liquid crystal is reoriented and dye molecules are directed along the field and a change in the selective absorption of the dye occurs[8].

The aim of this paper is to synthesize of some anthraquinone derivatives and examine the relationship between their chemical structures and spectroscopic properties.

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EXPERIMENTAL

2,6-Diaminoanthraquinone and other chemicals were obtained from Merck. All melting points were determined in sealed capillaries and are uncorrected. FT-IR and ^{1}H NMR spectra were recorded on a Mattson 1000 spectrometer as KBr pellets and a Varian Gemini 300 (300 MHz) NMR spectrometer in DMSO-d_6 or DMF-d_7, respectively. The mass spectra measurements were recorded on a Thermo Finnigan trace.

Synthesis

Diazotization of 2,6-diaminoanthraquinone: 2,6-Diaminoanthraquinone (1.44 g, 6.05×10^{-3} mol) was dissolved in 10 mL concentrated sulphuric acid. The solution was dripped into a solution of sodium nitrite (0.84 g, 0.0121 mol, in 5 mL water) which was cooled to 0-5 °C in salt-ice bath. After the mixture was stirred for 2 h in salt ice bath, the excess of nitrite was destroyed with urea and diazonium salt was suction filtered. The residue was added into 150 mL water and 50 g ice and the pH value was adjusted to four with sodium acetate[9].

Synthesis of 2,6-*bis*((4-hydroxyphenyl)diazenyl)anthracene-9,10-dione (1a): 2,6-Diaminoanthraquinone (1.44 g, 6.05×10^{-3} mol) was diazotized as described above. Phenol (1.2 g, 0.0121 mol), 5 g sodium carbonate was dissolved in 10 mL water and the mixture was cooled in salt-ice bath. The cold solution of diazotized amine was then dripped into this solution. The solution was suction filtered after two hours of stirring in salt-ice bath at room temperature. The residue was first washed with water then with methanol and dried. The product was recrystallized in DMF-ethanol mixture (2.0 g, yield 75 %). FT-IR (KBr, ν_{max}, cm^{-1}): 3403 (Ar-OH), 3063 (=C-H), 1650-1450 (-C=C-), 1670 (-C=O), 1580 (-N=N-), 1297 (=C-N). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 7-8.5 (m, Ar-H, 14H), 10.7 (s, Ar-OH, 2H). LC/MS (m/z): M$^+$ 448.

Synthesis of 2,6-*bis*((4-aminophenyl)diazenyl)anthracene-9,10-dione (1b): Aniline (1.2 mL, 0.0121 mol), 5 g sodium carbonate was dissolved in 10 mL water and the mixture was cooled in salt-ice bath. The diazonium salt of 2,6-diaminoanthraquinone (1.44 g, 6.05×10^{-3} mol) was dripped into this solution. The solution was suction filtered after 2 h of stirring in salt-ice bath at room temperature. The residue was first washed with water after that with methanol and then dried. (1.75 g, yield 65 %), m.p. 247-249 °C, FT-IR (KBr, ν_{max}, cm^{-1}): 3210 (-NH), 3063 (=C-H), 1664 (-C=O), 1650-1450 (-C=C-), 1573 (-N=N-), 1304 (=C-N). ^{1}H NMR (300 MHz, DMF-d_7, ppm) δ: 6.5-8.2 (m, Ar-H, 14H), 6.2 (s, -NH, 2H). LC/MS (m/z): (M+1)$^+$; 447.

Synthesis of 2,6-*bis*((2-aminophenyl-5-chlorophenyl)diazenyl)anthracene-9,10-dione (1c): *p*-Chloroaniline (1.2 mL, 0.0121 mol) and 5 g sodium carbonate were dissolved in 10 mL water and the mixture was cooled in a salt-ice bath. Then the diazonium salt of 2,6-diaminoanthraquinone (1.44 g, 6.05×10^{-3} mol) was dripped into this solution. The solution was suction filtered after 2 h of stirring in a salt-ice bath and 3 h at room temperature. The residue was firstly washed with water after that with methanol and dried. (2.1 g, yield 67 %). m.p. 262-265 °C, FT-IR (KBr, ν_{max}, cm^{-1}): 3204 (-NH), 3063 (=C-H), 1650-1450 (-C=C-), 1664 (C=O), 1573 (N=N), 1304 (=C-N). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 6.8-8.5 (m, Ar-H, 14H).

Synthesis of 2,6-*bis*((2-aminophenyl-5-iodophenyl)diazenyl)anthracene-9,10-dione (1d): *p*-Iodoaniline (1.2 mL, 0.0121 mol), 5 g sodium carbonate was dissolved in 10 mL water and the mixture was cooled in salt-ice bath. The diazonium salt of 2,6-diaminoanthraquinone (1.44 g, 6.05×10^{-3} mol) was dripped into this solution. The solution was filtered after 2 h of stirring in salt-ice bath at room temperature. The residue was first washed with water after that with methanol and then dried. (2.6 g, yield 62 %), m.p. 290-293 °C, FT-IR (KBr, ν_{max}, cm^{-1}): 3204 (-NH), 3063 (=C-H), 1664 (C=O), 1650-1450 (-C=C-), 1573 (N=N), 130, (=C-N), ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ: 6.8-8.5 (m, Ar-H, 14H).

Synthesis of 2,6-*bis*((4-methoxyphenyl)diazenyl)anthracene-9,10-dione (1e): Anisole (1.3 mL, 0.0121 mol), 5 g sodium carbonate was dissolved in 10 mL water and the mixture was cooled in a salt-ice bath. The diazonium salt of 2,6-diaminoanthraquinone (1.44 g, 6.05×10^{-3} mol) was dripped into this solution. The solution was filtered after 2 h of stirring in a salt-ice bath at room temperature. The residue was first washed with water after that with methanol and finally dried (1.9 g, yield 64 %). FT-IR (KBr, ν_{max}, cm^{-1}): 3063 (=C-H), 2921 (aliphatic -CH), 1676(C=O), 1650-1450 (-C=C-), 1587(N=N), 1297 (=C-N), 1247 (-C-O). The ^{1}H NMR spectrum of this product wasn't taken because suitable solvent could not be found for it.

Synthesis of 4,4'-(9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)*bis*-(diazene-2,1-diyl)*bis*(4,1-phenylene)diacetate (2a): Acetanhydride (0.5 mL, 0.005 mol) and 5 mL concentrated sulphuric acid were added onto **1a** (0.45 g, 0. 001 mol) and the mixture was stirred for 1 h at 50-60 °C. The mixture was cooled and 20 mL water was added. The residue was firstly washed with water, after that with methanol and dried. The product crystallized with DMF-ethanol mixture (0.71 g, yield 94 %), m.p. 258-260 °C, FT-IR (KBr, ν_{max}, cm^{-1}): 3063 (=C-H), 2921 (aliphatic -CH) , 1759 (-C=O), 1650-1450 (-C=C-), 1676 (C=O), 1320 (-C-O), 1592 (N=N), 1208 (=C-N), ^{1}H NMR (300 MHz, DMSO-d_6 and DMF-d_7, ppm) δ: 7,4-8,6 (m, Ar-H, 14H), 2,3 (s, $-CH_3$, 6H), LC/MS (m/z): $(M+1)^+$; 533.

Synthesis of 4,4'-(9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)*bis*-(diazene-2,1-diyl)*bis*(4,1-phenylene)dibenzoate (2b): 15 mL NaOH solution was added onto 2,6-*bis*(4-hydroxyphenyl)-diazenyl)anthracene-9,10-dione (0.45 g, 0.001 mol). Benzoyl chloride (0.5 mL, 0.004 mol) was added onto this mixture and it was shaken vigourously. The mixture was stirred for 1 h. The residue was filtered and washed with water and dried. (1.5 g, yield 82 %), m.p. 290-295 °C, FT-IR (KBr, ν_{max}, cm^{-1}): 3063 (=C-H), 1753 (-C=O), 1650-1450 (-C=C-), 1683 (C=O), 1592 (N=N), 1301 (=C-N), 1263 (-C-O), ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ: 7-8.7 (m, Ar-H), LC/MS (m/z): (M+1)$^+$; 657.

Synthesis of 2,6-*bis*((4'-propoxyphenyl)diazenyl)anthracene-9,10-dione (2c): 1a (0.45 g, 0.001 mol) was dissolved in absolute ethanol which contained equal amount of CH_3CH_2O-Na^+ 0.2 mL (0.002 mol). 1-Bromopropane was added onto this mixture and refluxed for 8 h. The mixture was cooled and filtered. The residue was washed with water followed by methanol and dried (0.34 g, yield 82 %), m.p. 275-278 °C). FT-IR (KBr, ν_{max}, cm^{-1}): 3063 (=C-H) , 2966-2877 (aliphatic -CH), 1650-1450 (-C=C-), 1676 (C=O), 1580 (N=N), 1304 (-C-O), 1289 (=C-N), ^{1}H NMR (300 MHz, DMSO-d_6 and DMF-d_7, ppm) δ: 7.1-8.6 (m, Ar-H, 14H), 4,1 (t, -OCH_2, 4H), 1,8 (m, -CH_2-, 4H), 1 (t, -CH_3, 6H), LC/MS (m/z): (M+1)$^+$; 533.

Synthesis of 2,6-*bis*((4-(hexyloxy)phenyl)diazenyl)anthracene-9,10-dione (2d): 1a (0.45 g, 0.001 mol) was dissolved in absolute ethanol which contained equal amount of $CH_3CH_2O^-Na^+$. 1-Bromohexane (0.3 mL, 0.002 mol) was added onto this mixture and refluxed for 8 h. The mixture was cooled and filtered. The residue was washed with water followed by methanol and dried (0.35 g, yield 57 %). FT-IR (KBr, ν_{max}, cm^{-1}): 3070 (=C-H), 2947-2864 (aliphatic -CH), 1650-1450 (-C=C-), 1676 (C=O), 1297 (-C-O), 1585 (N=N), 1297 (=C-N), ^{1}H NMR (500 MHz, DMSO-d_6 and DMF-d_7, ppm) δ: 7.1-8.6 (m, Ar-H, 14H), 4.1 (t, -OCH_2, 4H), 1.3-1.8 (m, -$CH_2CH_2CH_2CH_2$-, 16H), 0.9 (t, -CH_3, 6H), LC/MS (m/z) : (M-hexyl)$^+$; 531.

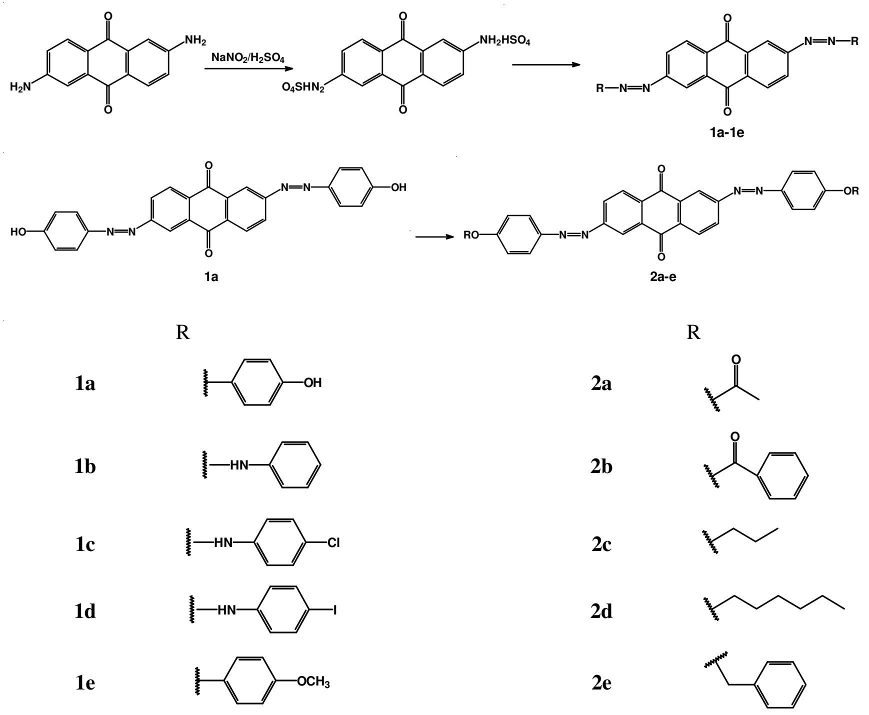
Synthesis of 2,6-*bis*((4-(benzyloxy)phenyl)diazenyl)anthracene-9,10-dione (2e): 1a (0.45 g, 0.001 mol) was dissolved in absolute ethanol which contain equal amount of $CH_3CH_2O^-Na^+$. Benzyl chloride (0.3 mL, 0.002 mol) was added onto this mixture and refluxed for 8 h. The mixture was cooled and filtered. The residue was washed with water followed by methanol and dried (0.45 g, yield 73 %), m.p. 241-243 °C. FT-IR (KBr, ν_{max}, cm^{-1}): 3070 (=C-H), 2921-2864 (aliphatic -CH), 1650-1450 (-C=C-), 1676 (C=O), 1587 (N=N), 1252 (=C-N), 1297 (-C-O), ^{1}H NMR (500 MHz, DMF-d_7, ppm) δ: 7.1-8.9 (m, Ar-H, 24H), 5.4 (s, -CH_2-, 4H), LC/MS (m/z): (M-phenyl)$^+$; 551.

RESULTS AND DISCUSSION

In this study, ten anthracenedione derivatives were synthesized consisting of **1c**, **1d**, **1e**, **2a**, **2b**, **2c**, **2d**, **2e** as new compounds. The compounds **1a** and **1b** were synthesized according to Coi *et al.* method[10] (yield 33.5 %, 14 %).

However, in this paper, compounds **1a** (yield 75 %) and **1b** (yield 65 %) were synthesized with more effective yield than Coi *et al*[10]. The result obtained by more effective yield is probably because of the pH of the media. As mentioned, pH of the media was adjusted after the completion of the reaction whereas in present study, pH was adjusted before the addition of coupling components. As a result pH may take an important role on these types of reactions.

The compounds were synthesized by different kinds of reactions such as diazotization coupling and SN reactions. The synthetic route to the synthesized compounds is shown in **Scheme-I**.



Scheme-I

The structures of synthesized compounds were identified on the basis of the FT-IR, ^{1}H NMR and MS spectral data. The spectral values support the expected structures. In FT-IR spectrum characteristic absorption peak of the hydroxy group was observed at 3403 cm^{-1} and NH_2 bands of diamino-9,10-anthraquinone were disappeared. In ^{1}H NMR spectrum, the peak of phenolic hydrogen of compound **1a** appeared at $\delta = 10.7$ ppm. OH band which was observed at 3403 cm^{-1} in the FT-IR spectrum of **1a** disappeared in the FT-IR spectra of **2a**, **2b**, **2c**, **2d** and **2e**. In addition, the FT-IR spectra of **2a** and **2b**, the characteristic strong bands observed at 1759 cm^{-1} indicated the stretching vibration of the C=O. The characteristic aliphatic C-H stretching vibration bands of **2a**, **2c**, **2d**, **2e** were approximately appeared at 2966-2877 cm^{-1}. Also characteristic NH_2 bands in FT-IR spectrum of 2,6-diamino-anthraquinone were not observed in the FT-IR spectra of **1a**, **1b**, **1c**, **1d** and **1e**. The existences of the azo groups were verified with the presence of bands in ranges of 1592-1573 cm^{-1}. In addition to ^{1}H NMR spectra of the synthesized compounds support the proposed structures. The MS spectral values are also compatible with the expected values.

The UV-Vis absorption spectra of the synthesized dyes were taken in acidic, basic and neutral media (Table-1). Generally, maximum wave length (λ_{max}) of the synthesized compounds increased in basic media but no changing occurred in acidic and neutral media.

TABLE-1
UV-VIS (λ_{amx}) VALUES OF THE DYES IN ACIDIC, BASIC AND NEUTRAL MEDIA

Product	λ_{max} (nm)		
	DMSO	Acid	Base
1a	399	394	629
1b	428	272	605
1c	348	271	446
1d	349	272	564
1e	261	274	262
2a	360	370	624
2b	371	371	624
2c	393	389	552
2d	390	269	552
2e	393	267	552

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