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Study of the Electric Properties of Azo/Hydrazone Tautomeric Mixture of the 4-(9-Anthrylazo)-1-naphthol

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Abstract: An azo/hydrazone mixture of the phenolic azo dye 4-(9-Anthrylazo)-1-naphthol was obtained in 58% yield. The product was characterized using spectroscopic techniques such as IR, NMR and ms. The electric conductivity of the tautomeric mixture was investigated in solid phase at ambient temperature. The electric measurements revealed that the azo derivative has an electric conductivity equals σ 0.657 × 10^{-7} Ω^{-1}cm^{-1} and electric resistivity ρ of 1.521545 × 10^{7} Ωcm which falls within the range of the semiconductors' electric resistivity that ranges between 10^{-2} and 10^{9} Ωcm.

Keywords: Azo/hydrazone mixture; Azo dye; Spectroscopic; Electric conductivity; Electric resistivity.

1. Introduction

Azo dyes have been of great interest of many research groups due to their stability, ease of synthesis and electrical properties [1, 2]. They provide a wide range of colors that depend on the number of azo groups and the substituents on the aryl moieties. These colors are originated from absorbing light in the visible region of the spectrum, making use of the delocalization of *n*- and π-electrons throughout their structures [1, 3]. Azo dyes have also been reported to possess electrical properties in which azo dyes could be used as semiconducting materials. The difference between semiconductors and good conductors could simply be described as follows; the resistance of the latter declines rapidly as the temperature decreases, whereas the resistance of semiconductors increases remarkably as the temperature falls down to the absolute zero [4]. The structure of the semiconductors allows electrical current to pass through and they possess electrical resistivity ranging between 10^{-2} Ωcm and 10^{9} Ωcm at room temperature [4-7]. The d.c. electric conductivity of azo dyes has been investigated [8]. The factors that are affecting the electric conductivity have been intensively studied by a number of research groups [1, 2, 9].

The electric conductivity σ of the synthesized 4-(*p*-aminophenylazo) benzene sulphonic acid was determined and found to be 0.917875 × 10^{-7} (Ωcm)$^{-1}$. The 4-(*p*-aminophenylazo) benzene sulphonic acid was reported to display a semiconducting behavior at 295 K as a pure material without the addition of a doping agent. The electric conductivity measurements revealed that the obtained azo dye, 4-(*p*-aminophenylazo) benzene sulphonic acid, possesses an electric resistivity ρ with a value of 1.089472779 × 10^{7} Ωcm which clearly comes within the resistivity range of the semiconducting materials [10].

2. Experimental

2.1. Materials

Nitric acid, hydrochloric acid, anthracene, sodium hydroxide, α-naphthol and methanol were purchased from Carlo Erba. Glacial acetic acid, sodium nitrite and sulfuric acid were purchased from Avonchem. Tin (II) chloride was purchased from PSPARK. DMSO was purchased from BDH Chemical. All chemicals were used without further purification.

2.2. Instrumentation

Melting points were measured on a Barnstead electrothermal IA 9100. Uv-vis absorptions were recorded on Uv-vis spectrophotometer-uv mini 1240-Shimadzu. PH was measured using Jenway PH meter 3505. ^{1}HNMR spectrum was recorded on a Bruker Avance 300 spectrometer. Residual proton signal from the deuteriated solvents were used as references [DMSO(^{1}H, 2.50ppm, ^{13}C, 39.51 ppm) and $CDCl_3$ (^{1}H, 7.24 ppm, ^{13}C, 77.23ppm)]. Coupling constants were measured in Hz. Infrared spectrum was recorded on Jasco FT/IR-4100 Fourier transform infrared spectrometer.

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Mass spectrum was recorded on a Micromass Autospec M spectrometer. Antifungal investigations were conducted using petri dishes 9.0 cm.

2.3. Preparation of 9-Nitroanthracene [11]

Concentrated nitric acid (4 cm^3) was added drop wise to a suspension of anthracene (10.00 g, 56.00 mmol) in glacial acetic acid (40 cm^3) maintaining the temperature below 30 ºC. This was stirred vigorously for 1 h to form a clear solution. A mixture of concentrated HCl (50 cm^3) and glacial acetic acid (50 cm^3) was added slowly to the reaction vessel resulting to a pale yellow precipitate of 9-nitro-10-chloro-9,10-dihydroanthracene. This was filtered, washed with glacial acetic acid (3 × 25 cm^3) and thoroughly with water until the washings were neutral. The resulting yellow solid was treated with warm solution (60 – 70 ºC) of 10% NaOH (200 cm^3), filtered, washed with warm water until the washing were neutral, air-dried and recrystallized from glacial acetic acid affording a fluffy yellow solid (7.94 g, 35.60 mmol, 64% yield); m.p 156 ºC (lit[12]. 148‒149 ºC, acetic acid); λ_{max} 448 nm ($CHCl_3$); FT-IR (KBr disc): 1511 cm^{-1} (C=C, aromatic), 1428 cm^{-1} ($Ar-NO_2$), 1278 cm^{-1} (C-N, aryl), δ_H (400 MHz; DMSO) 8.46 (1H, s, Ar-C*H*), 7.91 (2H, d, *J* = 8.70, Ar-C*H*), 7.83 (2H, d, *J* = 8.70, Ar-C*H*), 7.52 (2H, t, *J* = 15.11, Ar-C*H*), 7.44 (2H, t, *J* = 15.11, Ar-C*H*); δ_C (100 MHz; DMSO) 144.00 (1×Ar-*C*-NO_2), 134.00 (1×Ar-*C*), 130.41 (2 × Ar-*C*), 128.89 (2 × Ar-*C*) 127.92 (2 × Ar-*C*), 126.20 (2 × Ar-*C*), 122.64 (2 × Ar-*C*), 121.37 (2 × Ar-*C*); m/z ($C_{14}H_9NO_2$, Mwt. 223.23) 223.05 (43%), 197.88 (10%).

1.4. Preparation of 9-aminoanthracene 3 [12]

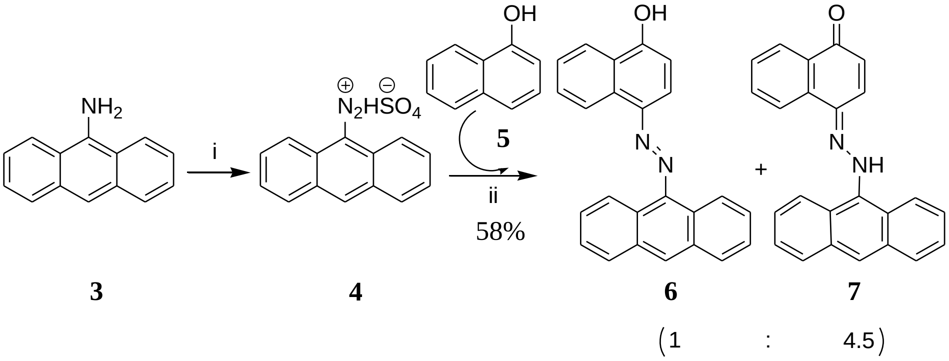
A suspension of 9-nitroanthracene (7.24 g, 32.50 mmol) in glacial acetic acid (145 cm^3) was heated to 70 – 80 °C for 1½ h. To the resulting clear solution was added slurry of $SnCl_2$ (31.00 g, 163.20 mmol) in concentrated HCl (110 cm^3) via dropping funnel. The resulting yellow precipitate was stirred at 80º C for a further ½ h, cooled to room temperature, filtered, washed with concentrated HCl (3×10 cm^3), treated with solution of 5% NaOH while manual stirring from time to time for 15 min, filtered, washed thoroughly with water until the washing were neutral and vacuum-dried at 50 ºC for 6 h to afford a yellow powder (4.90 g, 25.39 mmol, 87% yield). No further purification was required; m.p 160 ºC (lit[13] 153 ‒154 ºC, benzene); λ_{max} 420 nm ($CHCl_3$); FT-IR (KBr disc): 3463 cm^{-1} (N-H), 3412 cm^{-1} (N-H), 1588 cm^{-1} (C=C, aromatic), δ_H (400 MHz; $CDCl_3$) 8.55 (1H, s, Ar-C*H*), 8.29 (2H, m, Ar-C*H*), 7.99 –7.28 (4H, m, Ar-C*H*), 6.80 – 6.72 (2H, m, Ar-C*H*), 4.88 (2H, br s , Ar-NH_2); δ_C (100 MHz; DMSO) 134.18 (1×Ar-*C*-NH_2), 132.21 (2 × Ar-*C*), 129.00 (2 × Ar-*C*), 128.52 (2 × Ar-*C*), 127.27 (2 × Ar-*C*), 125.27 (2 × Ar-*C*), 123.85 (2 × Ar-*C*), 121.11 (1×Ar-*C*); m/z ($C_{14}H_{11}N$, Mwt. 193.24) 193.30 (100%), 192.23 (25%), 194.28 (20%).

1.5. Preparation of 4-[2-(anthracene9-yl)hydrazono]naphthalene-1(4H)-one 7

An adapted literature procedure was followed [13, 14] for synthesizing compound **7**. 9-aminoanthracene **3** (0.77 g, 8.00 mmol) was dissolved in concentrated sulfuric acid (25 cm^3). The resulting solution was cooled to 0 – 5 ºC, to which a precooled (0–5 ºC) aqueous solution of sodium nitrite (0.55 g, 8.00 mmol; in 30 cm^3 water) was added while stirring for 30 min maintaining the temperature between 0 – 5 ºC. An alkaline solution of the *α*-naphthol [0.58 g, 4.00 mmol; in 30 cm^3 of (2N NaOH and 2.5 g sodium carbonate)] was cooled to 0 – 5 ºC after which it was added to the reaction mixture. The reaction mixture was stirred for further 1½ h at 0–5 ºC. A dark brown precipitate was formed, filtered, washed with cold water (3×10 cm^3) and air dried. The crude material was recrystallized from glacial acetic acid, filtered, washed with water (3×10 cm^3) and air dried to give a mixture of two tautomers **72a** and **72b** (0.81g, 2.33 mmol, 58% yield) as a fine dark brown powder, m.p 290 ºC; λ_{max} 350 nm ($CHCl_3$); FT-IR (KBr disc): 3447 cm^{-1} (Ar-NH), 1644 cm^{-1} (C=O), 1580 cm^{-1} (C=N), 1314 cm^{-1} (C-N); δ_H (400 MHz; DMSO) 8.50 – 8.46 (1H, m, Ar-C*H*), 8.04 – 7.99 (2H, m, Ar-C*H*), 7.81 – 7.78 (1H, m, Ar-C*H*), 7.75 – 7.69 (2H, m, Ar-C*H*), 7.66 – 7.61 (2H, m, Ar-C*H*), 7.14 – 7.04 (4H, m, Ar-C*H*), 7.00 – 6.95 (1H, m, Ar-C*H*), 6.90 (1H, d, *J* = 8.60, C*H*), 6.70 (1H, d, *J* = 10.40, C*H*); m/z ($C_{24}H_{16}N_2O$, Mwt. 348.40) $[M-H_2O-H]^{-1}$ 328.12 (100%), 351.26 (37%), 334.05 (45%), 188 (47%), 172.13(97%). Selected peak for **72a**, δ_H (400 MHz; DMSO) 5.05 (1H, s, Ar-O*H*).

3. Results and Discussion

A mixture of two tautomers 6 and 7 was resulted in moderate yield through a coupling reaction between the 9-anthryl diazonium bisulfate **4** and an alkaline solution of *α*-naphthol **5 (Scheme 1)**.

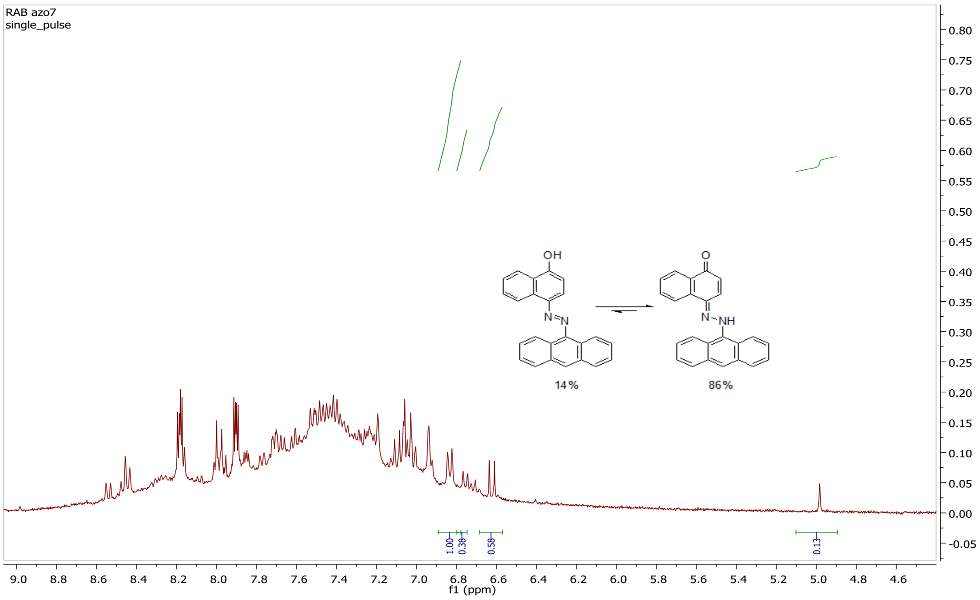


Reaction conditions and Reagents: (i) Conc. H_2SO_4, $NaNO_2$, 0–5 °C; (ii) aq. NaOH, 0–5 °C

Scheme 1: Coupling 9-anthryl diazonium bisulfate with the α-na

The ^{1}HNMR also showed distinctive doublet peaks for the aliphatic hydrogens of the *α,β*-unsaturated ketone in the hydrazone tautomer 7 (Fig. 1) with chemical shifts at 6.90 and 6.70 ppm with coupling constant of 8.6 Hz, 10.4 Hz respectively. Furthermore, the singlet peak of the phenolic hydroxyl group is seen at 5.05 ppm of the 4-(9-anthrylazo)-1-naphthol 6 provide that the formation of the expected hydrazone tautomer which is the major product (82%) and the phenolic azo tautomer as the minor product (18%).

Figure-1. ^{1}HNMR spectrum of the mixture of two tautomers 6 and 7



3.1. The Electric Measurements on the Mixture of 6 and 7 Tautomers

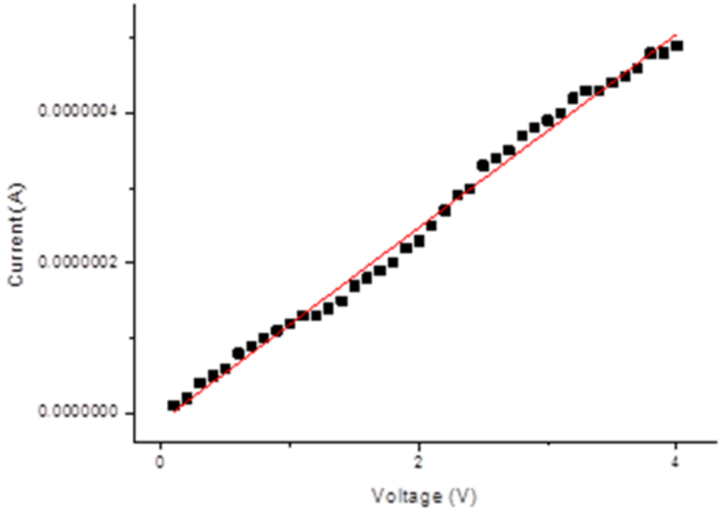
The voltage (0.1 – 4.0 V) was applied on the sample. The passed electrical current (I) through the sample was measured in μA (Table 1).

Table-1. The average values of applied voltage *vs* current

Voltage (V)	Current × 10^{-6} A	Voltage (V)	Current × 10^{-6} A	Voltage (V)	Current × 10^{-6} A	Voltage (V)	Current × 10^{-6} A
0.1	0.01	1.1	0.13	2.1	0.25	3.1	0.40
0.2	0.02	1.2	0.13	2.2	0.27	3.2	0.42
0.3	0.04	1.3	0.14	2.3	0.29	3.3	0.43
0.4	0.05	1.4	0.15	2.4	0.30	3.4	0.43
0.5	0.06	1.5	0.17	2.5	0.33	3.5	0.44
0.6	0.08	1.6	0.18	2.6	0.34	3.6	0.45
0.7	0.09	1.7	0.19	2.7	0.35	3.7	0.46
0.8	0.10	1.8	0.20	2.8	0.37	3.8	0.48
0.9	0.11	1.9	0.22	2.9	0.38	3.9	0.48
1.0	0.12	2.0	0.23	3.0	0.39	4.0	0.49

A linear relationship between the applied voltage and the passed electrical current was obtained by processing the experimental data using Origin 8.1 (Fig. 2).

Figure-2. Current vs applied voltage correlation using Origin 8.1 software



Since the resistance R could be obtained from the reverse of the slope of the equation **1**.

$$y = a + bx \qquad \textbf{(1)}$$

$$\therefore R = \frac{1}{1.2898 \times 10^{-7}\Omega^{-1}} = 0.77531 \times 10^{7}\Omega \qquad \textbf{(2)}$$

The resistivity of the tautomeric mixture could be calculated by following equation **3**

$$\rho = R\frac{A}{l} \qquad \textbf{(3)}$$

Where $\frac{A}{l}$ is a constant equals 1.9625 cm.

$$\therefore \rho = 0.77531 \times 10^{7}\,\Omega \times 1.9625\,cm = 1.521545 \times 10^{7}\,\Omega cm$$

The electric conductivity σ of this azo/hydrazone **6/7** is:

$$\sigma = \frac{1}{\rho} = \frac{1}{1.521545 \times 10^{7}\Omega cm} = 0.657226 \times 10^{-7}\Omega^{-1}cm^{-1} \qquad \textbf{(5)}$$

4. Conclusion

A tautomeric azo/hydrazone mixture of the 4-(9-Anthrylazo)-1-naphthol was formed in moderate yield. The electric measurements showed that this azo derivative possesses an electric resistivity ρ of 1.521656 × 10^7 Ωcm by which it could be classified as a semiconductor.

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