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Synthesis and Electric Conductivity Study of the New Azo Dye 4-(9-Anthrylazo) Phenol

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Abstract:
A phenolic azo dye, 4-(9-anthrylazo) phenol, has been synthesized and its spectroscopic properties were studied. According to the spectroscopic study, the synthesized azo dye is thought to be existing as two tautomers which are the azo phenol tautomer and the hydrazo keto tautomer. This finding was supported by the fact that the vibrational band of the phenolic hydroxyl group was seen at 3480 cm^{-1} along with the absorption band of an α,β-unsaturated ketone at 1700 cm^{-1} and the azo vibrational band at 1540 cm^{-1} in the IR spectrum. The DC electric conductivity of the resulting dye was determined and its electric resistivity was found to be within the range of the semiconductors.

Keywords: azo dye, synthesized, spectroscopic, tautomers, DC electric conductivity, semiconductors.

I. Introduction

Dyes are aromatic compounds absorb light of wavelength ranging between 700 – 350 nm.[1,2] The colors of these dyes are originated by absorbing the light in the visible region of the spectrum due to the delocalization of *n*- and *π*-electrons throughout their structures.[3,4] The difference between semiconducting and good conducting materials is that the resistance of the good conductors declines rapidly as the temperature drops off, whereas the resistance of semiconductors increases notably as the temperature falls down to the absolute zero.[5] The structure of the semiconductors tolerates electrical current to pass through and they possess electrical resistivity ranging from 10^{-2} to 10^{9} Ω-cm at room temperature.[5,6,7,8] The d.c. electric conductivity of azo dyes has been investigated by a number of research groups.[9,10] Herein the spectroscopic and the electric properties of the 4-(9-anthrylazo) phenol were studied.

II. Experimental

Materials

Phenol, nitric acid and hydrochloric acid were purchased from Carloerba, sulphuric acid from Avonchem, sodium nitrite from Riedel-Dehean. The anthracene was obtained from CODEX, stannous chloride was purchased from Ps Park. These chemicals were used without further purification.

Instrumentation

Melting point was measured on a UK Bamstead/Electro thermal-9200 apparatus and is uncorrected. Uv-vis absorptions were recorded on Uv-vis spectrophotometer-uv mini 1240-Shimadzu. pH was measured using Jenway pH meter 3505. ^{1}H NMR spectrum was recorded on a Bruker Avance 300 spectrometer. Residual proton signals from the deuteriated solvents were used as references [DMSO (^{1}H, 2.50 ppm) and $CDCl_3$ (^{1}H, 7.26 ppm]. Coupling constants were measured in Hz. Infrared spectrum was recorded on Jasco FT/IR-4100 Fourier transform infrared spectrometer. Mass spectrum was recorded on a Micromass Autospec M spectrometer. The electric measurements were carried out using Laboratory power supply EA-PS 2016-050. The electrical current was measured in μA units by the use of CEM/DT-3900 ammeter. The applied voltage was determined in V units by employing Peak Tech 2010 DMM voltmeter.

Preparation of 9-Nitroanthracene 2 [11]

Concentrated nitric acid (4 cm^3) was added dropwise to a suspension of anthracene (10.0 g, 56.0 mmol) in glacial acetic acid (40 cm^3) maintaining the temperature below 30 °C. 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 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 a warm solution (60 – 70 °C) of 10% NaOH (200 cm^3), filtered, washed with warm water until the washings were neutral, air-dried and recrystallised from glacial acetic acid affording a fluffy yellow solid (8.31 g, 67% yield), mp 153 – 157 °C (acetic acid) (lit.[11] 148 – 149 °C acetic acid); δ_H (250 MHz; $CDCl_3$) 8.59 (1H, s, Ar-C*H*), 8.03 (2H, d, *J* 7.6, Ar-C*H*), 7.92 (2H, d, *J* 7.6, Ar-C*H*), 7.68 – 7.52 (4H, m, Ar-C*H*); δ_C (62.5 MHz; $CDCl_3$) 130.7 (Ar-*C*-NO_2), 130.4 (2 × Ar-*C*), 128.9 (2 × Ar-*C*), 128.4 (Ar-

C), 126.2 (2 × Ar-C), 122.6 (2 × Ar-C), 121.3 (4 × Ar-C). NMR data was in accordance with the literature.

Preparation of 9-Aminoanthracene 3 [12]

A suspension of 9-nitroanthracene (7.24 g, 32.5 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 $SnCl_2$ (31.0 g, 163.2 mmol) in concentrated HCl (110 cm^3) *via* a dropping funnel. The resulting yellow precipitate was stirred at 80 °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 for approximately 15 min with manual stirring from time to time, filtered, washed thoroughly with water until the washings were neutral and vacuum-dried at 50 °C for 6 h to afford a yellow powder (5.18 g, 83% yield). No further purification was required, mp 165 – 170 °C (lit.[12] 153 – 154 °C, benzene); δ_H (250 MHz; $CDCl_3$) 7.90 (4H, m, Ar-C*H*), 7.85 (1H, s, Ar-C*H*), 7.43 (4H, m, Ar-C*H*), 4.85 (2H, br s, N*H*$_2$); δ_C (62.5 MHz; $CDCl_3$) 129.0 (2 × Ar-*C*), 125.2 (4 × Ar-*C*), 123.8 (2 × Ar-*C*), 121.1 (2 × Ar-*C*), 116.3 (4 × Ar-*C*). NMR data was in accordance with the literature.

Preparation of 4-(9-anthrylazo)phenol 5

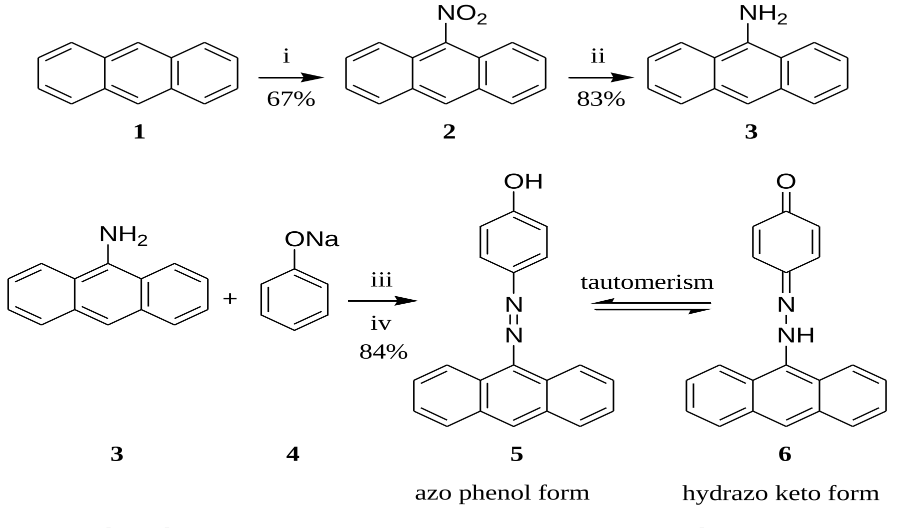
An addapted literature proceedure[13] was followed towards the preparation of 4-(9-anthrylazo)phenol. A solution of 9-aminoanthracene (1.93 gm, 10 mmol) in 2 *N* sulphuric acid (40 cm^3) was cooled down to 0 – 5 °C. A precooled aqueous solution (0 – 5 °C) of sodium nitrite (0.69 gm, 10 mmol in 10 cm^3 water) was added slowly to the cooled acidic 9-aminoanthracene solution maintaining the temperature at 0 – 5 °C while stirring for 30 min. An alkaline cold solution (0 – 5 °C) of phenol (0.94 gm, 10 mmol) in 1N sodium hydroxide (10 cm^3) was added to the reaction mixture with a continuous stirring at 0 – 5 °C for 1½ hr. A brown precipitate of the desired azo dye was formed, filtered, washed with distilled water until the filtrate became neutral and air-dried to give the azo product as a dark brown powder (2.51 gm, 8.42 mmol, 84% yield); mp 156 °C. uv-vis ($CHCl_3$) 390.0, 369.0, 242.0 nm; IR ν_{max} (KBr)/cm^{-1}; 3480 (br), 1700 (m), 1540 (m), 1278 (s). δ_H [300 MHz; $(CD_3)_2SO$] 8.24 – 8.21 (1H, m, Ar-C*H*); 7.95 – 7.92 (2H, m, Ar-C*H*); 7.77 – 7.73 (2H, m, Ar-C*H*); 7.48 – 7.27 (4H, m, Ar-C*H*); 7.07 – 6.70 (2H, m, C*H*); 6.58 – 6.56 (2H, m, C*H*), 5.01 (1H, s, N*H*). m/z EI$^+$ ($C_{20}H_{14}N_2O$, 298.34) 74 (100), 76 (43), 99 (13), 109 (01), 125 (08), 1150 (03), 164 (93), 178 (01)193 (5), 209 (02), 234 (0.04), 248 (0.1), 298 (0.03).

Procedure for Electric Measurements

An adapted literature procedure was followed.[14,15] The sample of the azo dye **5** (with a radius of 0.25 cm and thickness of 0.1 cm) was placed between two copper electrodes one of which was connected to a power source and the other copper electrode was connected to an ammeter to measure the electrical current. The electric measurements were carried out at 295 K.

III. Results and Discussion

The synthesis of 4-(9-anthrylazo) phenol **5** was started with the preparation of 9-nitroanthracene **2**, in good yield (67%), *via* a nitration reaction of the anthracene **1**.[11] The resulting 9-nitroanthracene **2** was then reduced by the use of a slurry of $SnCl_2$ in concentrated HCl to form the corresponding 9-aminoanthracene **3** in very good yield (83%).[12] The targeted azo dye **5** was synthesized by coupling the diazonium bisulphate salt of the 9-aminoanthracene **3** and the sodium phenoxide **4** at 0 – 5 °C affording a satisfactory reaction yield, 84%, of the desired azo dye **(Scheme 1)**. The resulting azo dye **5** was found to absorb uv light at 390.0, 369.0 and 242.0 nm in chloroform.[16]



Reagents and conditions: (i) conc. HNO_3, HOAc, <30 °C, conc. HCl/HOAc, stirring, 1 h; (ii) slurry of $SnCl_2$ in conc. HCl, HOAc, stirring, 70 - 80 °C, 1.5 h; (iii) aq. $NaNO_2$, conc. H_2SO_4, 0 - 5 °C, 30 min; (iv) stirring, 0 - 5 °C, 1.5 h

Scheme 1: synthesis of 4-(9-anthrylazo) phenol 5

The IR spectrum of the product indicated that the targeted azo dye 4-(9-anthrylazo) phenol **5** was formed as the vibrational band for the –N=N– group was clearly seen at around 1540 cm^{-1} and an absorption band for the vibration of phenolic OH group at about 3480 cm^{-1}. Despite observing the vibraional band for the azo group –N=N–, a rather sharp absorption band for an α,β-unsaturated ketone was seen at about 1700 cm^{-1}. This indicates the existence of the haydrazo keto tautomer **6** besides the azo counterpart **5 (Fig. 1)**.

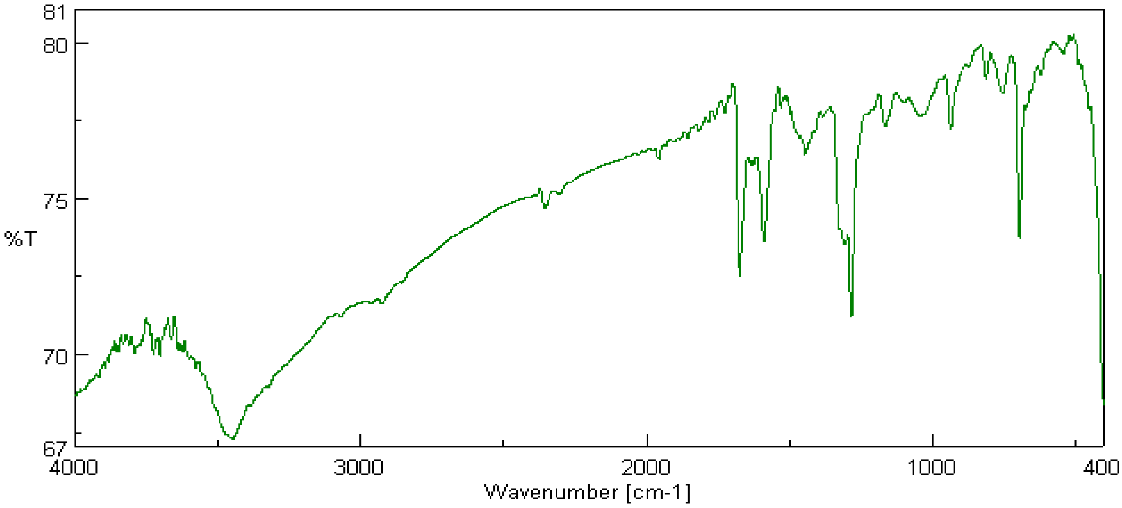


Figure 1: the IR of 4-(9-anthrylazo) phenol 5

The electric behavior of the 4-(9-anthrylazo) phenol **5** was investigated in the solid phase at 295 K. A pellet of the azo dye **5**, with a radius of 0.25 cm and a thickness of 0.1 cm, was placed between two copper electrodes and subjected to a voltage starting from 0.1 to 4.0 volt. The electrical current that passed through the azo dye pellet was measured at 295 K **(Table 1)**.

V	**$A \times 10^{-6}$**	**V**	**$A \times 10^{-6}$**	**V**	**$A \times 10^{-6}$**	**V**	**$A \times 10^{-6}$**
0.1	0.01	1.1	0.11	2.1	0.21	3.1	0.32
0.2	0.02	1.2	0.12	2.2	0.22	3.2	0.33
0.3	0.03	1.3	0.13	2.3	0.24	3.3	0.34
0.4	0.04	1.4	0.14	2.4	0.24	3.4	0.36
0.5	0.06	1.5	0.16	2.5	0.26	3.5	0.36
0.6	0.06	1.6	0.17	2.6	0.26	3.6	0.37
0.7	0.07	1.7	0.18	2.7	0.27	3.7	0.38
0.8	0.08	1.8	0.18	2.8	0.29	3.8	0.39
0.9	0.10	1.9	0.19	2.9	0.30	3.9	0.39
1.0	0.11	2.0	0.21	3.0	0.31	4.0	0.41

Table 1: Experimental data of applied voltage (V) vs measured current (A)

This experimental data was processed by *ORIGIN 8.1* in which the correlation between the applied voltage and the measured electrical current was found to be linear relationship **(Fig. 2)** and following the **(Equation 1)**.

$$y = a + bx \qquad (1)$$

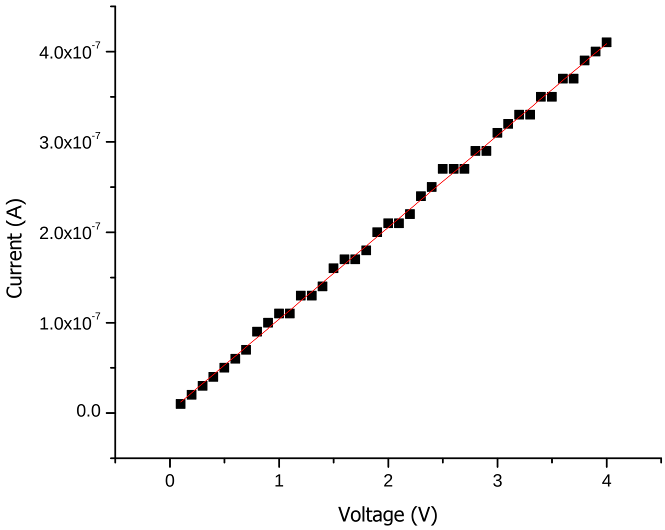


Figure 2: current vs applied voltage correlation using Origin 8.1 software

The resistance R equals the reverse of the slope (the slope = $1.0167 \times 10^{-7}\,\Omega^{-1}$) **(Equation 2)**.

$$R = \frac{1}{1.0167 \times 10^{-7}\Omega^{-1}} = 0.98357 \times 10^{7}\,\Omega \qquad (2)$$

The electric resistivity ρ of the azo dye **5** could easily be determined **(Equation 3)**.

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

Where A is the surface area of the sample pellet and equals πr^2 (r = 0.25 cm), whereas l is the thickness of the sample pellet and equals 0.1 cm **(Equation 4)**.

Therefore;

$$\frac{A}{l} = \frac{\pi r^2}{l} = \frac{3.14 \times (0.25\,cm)^2}{0.1\,cm} = 1.9625\,cm \qquad (4)$$

$$\therefore\ \rho = 0.98357 \times 10^{7}\,\Omega \ \times 1.9625\text{ cm}$$
$$= 1.930256 \times 10^{7}\,\Omega\text{ cm} \qquad (5)$$

The electric resistivity ρ **(Equation 5)** of the azo dye **5** comes within the range of the semiconductors' electric resistivity which it is between 10^{-2} and 10^{9} Ωcm.[5]

The electric conductivity σ of the azo dye **5**, therefore, could easily be calculated **(equation 6)**.

$$\sigma = \frac{1}{\rho} = 0.518066 \times 10^{-7}\,\Omega^{-1}\,\text{cm}^{-1} \qquad (6)$$

IV. Conclusions

The azo dye, 4-(9-anthrylazo) phenol **5**, was synthesized in very good yield and its spectroscopic properties were investigated. A tautomerism was found to be taking place in which the 4-(9-anthrylazo) phenol **5** is thought to be existing in two tautomeric forms which are the hydrazo keto form **6** and the azo phenol form **5**. The electric conductivity study revealed that the azo dye **5** could be classified as a semiconducting material possessing an electric resistivity ρ of 1.930256 × 10^{7} Ωcm which is within the range of the electric resistivity of semiconductors (10^{-2} – 10^{9} Ωcm).

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