Synthesis and Electric Conductivity Study of 4-(*p*-Aminophenylazo) Benzene Sulphonic Acid

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Abstract: An azo dye derived from sulphanilic acid was synthesized in moderate yield by a coupling reaction between a diazonium salt of the sulphanilic acid and aniline at 0-5 °C. The resulting azo derivative was characterized using nuclear magnetic resonance (NMR) and various spectroscopic methods such as uv-vis, infrared radiation (IR) and ms. The electric conductivity σ of the resulting 4-(*p*-aminophenylazo) benzene sulphonic acid was determined and found to be $0.917875 \times 10^{-7} (\Omega\text{-cm})^{-1}$. The 4-(*p*-aminophenylazo) benzene sulphonic acid showed a semiconducting behavior at 295 K without the need of adding a doping agent. The electric conductivity measurements revealed that the synthesized 4-(*p*-aminophenylazo) benzene sulphonic acid possesses an electric resistivity ρ of $1.089472779 \times 10^7 \Omega\text{-cm}$ which renders this azo dye a semiconducting material.

Key words: Azo dye, synthesized, electric conductivity, semiconducting.

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 colours 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]. The main difference between semiconductors and good conductors is that 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 $10^{-2} \Omega\text{-cm}$ and $10^9 \Omega\text{-cm}$ 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]. Here in, an azo dye, 4-(*p*-aminophenylazo) benzene sulphonic acid, has been synthesized and its electric conductivity at 295 K has also been determined.

2. Materials and Methods

2.1 Materials

Sulphanic acid, sulphuric acid and sodium nitrite were purchased from Riedel-Dehean. The aniline was obtained from Hassco Belgium. These chemicals were used without further purification.

2.2 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. ^1H NMR spectrum was recorded on a Bruker Avance 300 spectrometer. Residual proton signals from the deuteriated solvents were used as references [DMSO

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(^1H , 2.50 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.

2.3 Preparation of 4-(*p*-aminophenylazo) benzene sulphonic acid 3

An adapted literature procedure [10], was followed towards the synthesis of the azo derivative 3. A solution of sulphanilic acid (3.72 g, 20 mmol) in 2 N sulphuric acid (272 cm^3) was cooled down to 0-5 $^\circ\text{C}$. An aqueous solution of sodium nitrite (5.44 g, 2.54 mmol in 22 cm^3 water) was added slowly to the cooled sulphanilic acid solution maintaining the temperature at 0-5 $^\circ\text{C}$ while stirring. Freshly purified aniline (2.00 g, 20 mmol) was then added to the reaction mixture with a continuous stirring at 0-5 $^\circ\text{C}$ for 30 min. The reaction mixture was left standing overnight at room temperature after which the reaction mixture was treated by a solution of ammonium hydroxide (8 cm^3 , 2 N) raising the pH up to about 6. A reddish brown precipitate of the desired azo dye was formed, filtered and air-dried to give 62% yield of the azo derivative 3 (3.69 g, 21.52 mmol). No further purification was required. mp 290 $^\circ\text{C}$ (dec); UV (*n*-propyl alcohol) 434.0 nm; IR (KBr) vcm^{-1} , 3,336 (NH_2), 1,417 ($\text{N}=\text{N}$), 1,020 ($\text{S}=\text{O}$). ^1H HNMR δ_{H} [300 MHz; (CD_3) $_2\text{SO}$] 7.82-7.76 (6H, m, ArH); 6.96-6.93 (2H, m, ArH); 3.40 (3H, br s, NH_2 and SO_3H). MS m/z EI^+ ($\text{M}+1$, $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_3\text{S}$, 278.06) 279 (17), 278 (35), 144 (260), 143 (22), 93 (100), 81 (35), 80 (83), 64 (70).

2.4 General Procedure for Measuring the Electric Current

An adapted literature procedure was followed [11, 12].

The sample of the azo dye 3 (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.

3. Results and Discussion

The 4-(*p*-aminophenylazo) benzene sulphonic acid 3 was synthesized from a coupling reaction between the diazonium bisulphate salt of the sulphanilic acid 1 and the aniline 2 at 0-5 $^\circ\text{C}$ (Scheme 1). The wavelength for the uv-vis absorption of the resulting azo dye 3 was measured and found to be 434.0 nm in *n*-propyl alcohol.

The IR spectrum also showed the vibrational band of the azo group at 1,417 cm^{-1} [10, 13].

A packed pellet of the azo dye 3, 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 ranging between 0.1-4.0 V. The passed electrical current through the azo dye pellet, at 295 K, was measured in Table 1.

These experimental results were processed by ORIGIN 8.1 and it was found that the correlation between the applied voltage and the measured current is linear relationship (Fig. 1) following the Eq. (1).

Reagents and conditions: (i) aq. NaNO_2 , conc. H_2SO_4 , 0 - 5 $^\circ\text{C}$, 1 h; (ii) stirring, 0 - 5 $^\circ\text{C}$, 30 min, then rt, 24 h

Scheme 1 Synthesis of 4-(*p*-aminophenylazo) benzene sulphonic acid 3.

Table 1 V = the applied voltage value in volt unit; A= the measured current in ampere unit.

V	A $\times 10^{-7}$	V	A $\times 10^{-7}$	V	A $\times 10^{-7}$
0.1	0.1	1.3	2.3	2.9	5.1
0.2	0.2	1.4	2.5	3.0	5.3
0.3	0.4	1.5	2.7	3.1	5.5
0.4	0.6	1.6	2.8	3.2	5.7
0.5	0.8	1.7	2.9	3.3	5.9
0.6	0.9	1.8	3.1	3.4	6.1
0.7	1.1	1.9	3.3	3.5	6.3
0.8	1.3	2.0	3.5	3.6	6.5
0.9	1.5	2.1	3.8	3.7	6.6
1.0	1.7	2.2	3.9	3.8	6.7
1.1	1.9	2.3	4.1	3.9	6.8
1.2	2.1	2.4	4.2	4.0	6.9

Fig. 1 The IR spectrum of the azo dye 3. **Fig. 2** The applied voltage (V) vs. current (A).

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

The resistance R equals the reverse of the slope (slope = $1.80133 \times 10^{-7} \Omega^{-1}$) (Eq. (2)):

$$R = \frac{1}{1.80133 \times 10^{-7} \Omega^{-1}} \quad (2)$$

$$\therefore R = 5.55145365 \times 10^6 (\Omega)$$

The electric resistivity ρ of the azo dye 3 could easily

be determined Eq. (3).

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

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:

$$\frac{A}{l} = \frac{\pi r^2}{l} \quad (4)$$

$$\therefore \frac{A}{l} = \frac{3.14 \times (0.25 \text{ cm})^2}{0.1 \text{ cm}} = 1.9625 \text{ cm}$$

$$\therefore \rho = 5.55145365 \times 10^6 \Omega \times 1.9625 \text{ cm} \quad (5)$$

$$\rho = 1.089472779 \times 10^7 \Omega \cdot \text{cm}$$

The electric resistivity ρ (Eq. (5)) of the azo dye 3 comes within the range of the semiconductors' electric resistivity which is between $10^{-2} \Omega \cdot \text{cm}$ and $10^9 \Omega \cdot \text{cm}$ [4]. Therefore, the electric conductivity σ of the azo dye 3 could easily be calculated .:

$$\sigma = \frac{1}{\rho} = 0.917875 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1} \quad (6)$$

4. Conclusions

The azo dye, 4-(*p*-aminophenylazo) benzene sulphonic acid 3, was synthesized in rather good yield. This azo dye was characterized using various spectroscopic techniques. The electric conductivity study on this azo dye revealed that the 4-(*p*-aminophenylazo) benzene sulphonic acid 3 could be classified as a semiconductor with an electric resistivity ρ of $1.089472779 \times 10^7 \Omega \cdot \text{cm}$ which is within the range of the semiconducting materials.

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