

Study of the Azo Hydrazone Tautomerism in the 4-(9-Anthrylazo) Phenol

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Abstract—The spectroscopic study on 4-(9-anthrylazo) phenol has revealed that the azo dye under study exists in two tautomeric forms which are azo phenol and hydrazone keto forms in ratio of almost (1:1). The azo hydrazone tautomerism was confirmed by the use of IR spectroscopy and HNMR in which the characteristic absorption bands and chemical shifts for both tautomers were assigned.

Keywords—Spectroscopic, tautomeric forms, azo hydrazone tautomerism, IR spectroscopy, HNMR.

I. INTRODUCTION

DYES are aromatic compounds absorb light of wavelength ranging between 700–350nm.[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 use of azo dyes in textile, food, paper printing, cosmetic and electronic industries has remarkably been increased and also attracted great attention on the synthesis, characterization, purification and their applications. [5]-[11] The azo dyes with at least one conjugated protic group with the azo group shows azo hydrazone tautomerism. [12]

Herein the spectroscopic study of the 4-(9-anthrylazo) phenol was carried out in which the tautomerism process was investigated.

II. EXPERIMENTAL

A. 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.

B. 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 (^1H , 2.50 ppm) and CDCl_3 (^1H , 7.26ppm)]. 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.

C. Preparation of 9-Nitroanthracene [13]

Concentrated nitric acid (4cm^3) was added dropwise to a suspension of anthracene (10.0g, 56.0mmol) in glacial acetic acid (40cm^3) maintaining the temperature below 30°C . This was stirred vigorously for 1h to form a clear solution. A mixture of concentrated HCl (50cm^3) and glacial acetic acid (50cm^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 ($3 \times 25\text{cm}^3$) 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 (200cm^3), filtered, washed with warm water until the washings were neutral, air-dried and recrystallised from glacial acetic acid affording a fluffy yellow solid (8.31g, 67% yield), mp 153 – 157°C (acetic acid) (lit.¹³ 148 – 149°C acetic acid); δ_{H} (250MHz; CDCl_3) 8.59 (1H, s, Ar-CH), 8.03 (2H, d, J 7.6, Ar-CH), 7.92 (2H, d, J 7.6, Ar-CH), 7.68–7.52 (4H, m, Ar-CH); δ_{C} (62.5 MHz; CDCl_3) 130.7 (Ar-C- NO_2), 130.4 ($2 \times$ Ar-C), 128.9 ($2 \times$ Ar-C), 128.4 (Ar-C), 126.2 ($2 \times$ Ar-C), 122.6 ($2 \times$ Ar-C), 121.3 ($4 \times$ Ar-C). NMR data was in accordance with the literature.

D. Preparation of 9-Aminoanthracene [13]

A suspension of 9-nitroanthracene (7.24g, 32.5mmol) in glacial acetic acid (145cm^3) was heated to 70 – 80°C for $1\frac{1}{2}$ h. To the resulting clear solution was added slurry of SnCl_2 (31.0g, 163.2mmol) in concentrated HCl (110cm^3) via a dropping funnel. The resulting yellow precipitate was stirred at 80°C for a further $\frac{1}{2}$ h, cooled to room temperature, filtered, washed with concentrated HCl ($3 \times 10\text{cm}^3$), treated with solution of 5% NaOH for approximately 15min with manual stirring from time to time, filtered, washed thoroughly with water until the washings were neutral and vacuum-dried at 50°C for 6h to afford a yellow powder (5.18g, 83% yield). No further purification was required, mp 165 – 170°C (lit.¹³ 153 – 154°C , benzene); δ_{H} (250 MHz; CDCl_3) 7.90 (4H, m, Ar-CH), 7.85 (1H, s, Ar-CH), 7.43 (4H, m, Ar-CH), 4.85 (2H, br s, NH_2); δ_{C} (62.5 MHz; CDCl_3) 129.0 ($2 \times$ Ar-C), 125.2 ($4 \times$ Ar-C), 123.8 ($2 \times$ Ar-C), 121.1 ($2 \times$ Ar-C), 116.3 ($4 \times$ Ar-C). NMR data was in accordance with the literature.

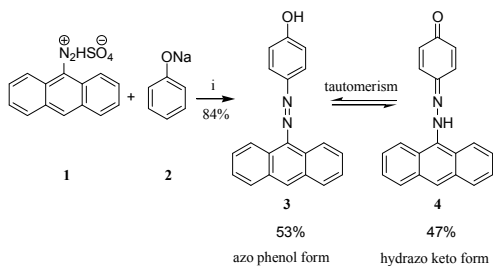
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E. Preparation of 4-(9-Anthrylazo)phenol 3 and 4-[2-(Anthracen-9-yl)hydrazono]cyclohexa-2,5-dienone 4 [13], [14], [15]

A solution of 9-aminoanthracene (1.93gm, 10mmol) in 2 N sulphuric acid (40cm³) was cooled down to 0–5°C. A precooled aqueous solution (0–5°C) of sodium nitrite (0.69 gm, 10mmol in 10cm³ water) was added slowly to the cooled acidic 9-aminoanthracene solution maintaining the temperature at 0–5°C while stirring for 30min. An alkaline cold solution (0–5°C) of phenol (0.94gm, 10mmol) in 1N sodium hydroxide (10cm³) was added to the reaction mixture with a continuous stirring at 0–5°C for 1½hr. 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 product as a dark brown powder (2.51gm, 8.42mmol, 84% yield); mp 156°C (lit¹³ 156°C). Uv-vis (CHCl₃) 390.0, 369.0, 242.0nm; IR ν_{\max} (KBr)/cm⁻¹: 3480 (br), 1700 (m), 1540 (m), 1278 (s). δ_H [300 MHz; (CD₃)₂SO] 8.24 – 8.21 (1H, m, Ar-CH); 7.95 – 7.92 (2H, m, Ar-CH); 7.77 – 7.73 (2H, m, Ar-CH); 7.48 – 7.27 (4H, m, Ar-CH); 7.07 – 6.70 (2H, m, Ar-CH); 6.58 – 6.56 (2H, m, CH), 5.04 (1H, s, OH). m/z EI⁺ (C₂₀H₁₄N₂O, 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).

III. RESULTS AND DISCUSSION

The synthesis of 4-(9-anthrylazo) phenol **3** was started with the preparation of 9-nitroanthracene, in good yield (67%), via a nitration reaction of the anthracene. The resulting 9-nitroanthracene was then reduced by the use of a slurry of SnCl₂ in concentrated HCl to form the corresponding 9-aminoanthracene in very good yield (83%).^[13] The targeted azo dye **3** was synthesized by coupling the 9-anthryldiazonium bisulphate **1** and the sodium phenoxide **2** at 0–5 °C affording a satisfactory reaction yield, 84%, of the desired azo dye (Fig. 1). [13] The resulting azo dye **3** was found to absorb uv light at 390.0, 369.0 and 242.0 nm in chloroform.



Reagents and conditions: (i) aq. NaNO₂, conc. H₂SO₄, 0 – 5 °C, 30 min; then stirring, at 0 – 5 °C, 1.5 h

Fig. 1 Synthesis of 4-(9-anthrylazo) phenol 3

The IR spectrum of the product indicated that the targeted azo dye 4-(9-anthrylazo) phenol **3** along with its counterpart tautomer 4-[2-(anthracen-9-yl)hydrazono]cyclohexa-2,5-dienone **4** were formed. The vibrational band for the –N=N– group was clearly seen at around 1540cm⁻¹ and an absorption band for the vibration of phenolic OH group at about 3480cm⁻¹

¹. A rather sharp absorption band for an α,β -unsaturated ketone was also seen at about 1700 m⁻¹. This indicates the existence of the haydrazo keto tautomer **4** besides the azo phenol counterpart **3** throughout an expected tautomerism process in such systems (Fig. 2).

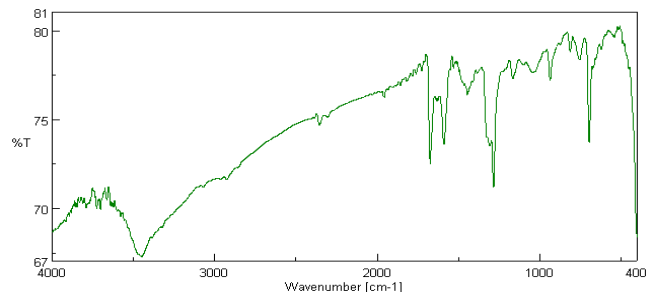


Fig. 2 IR spectrum for the mixture of the two tautomers 3 and 4

The formation of the two expected tautomers **3** and **4** was further confirmed by the proton NMR of the product, which shows two doublets 5.70 ppm and 5.59 ppm for the four aliphatic protons of the α,β -unsaturated ketone along with the singlet signal for the phenolic hydroxyl group at 5.04 ppm (Fig. 3). The 4-(9-anthrylazo) phenol **3** and the 4-[2-(anthracen-9-yl)hydrazono]cyclohexa-2,5-dienone **4** were formed in ratio of almost (1:1) yielding 53% of the phenol azo tautomer **3** and 47% of the other tautomer **4**.

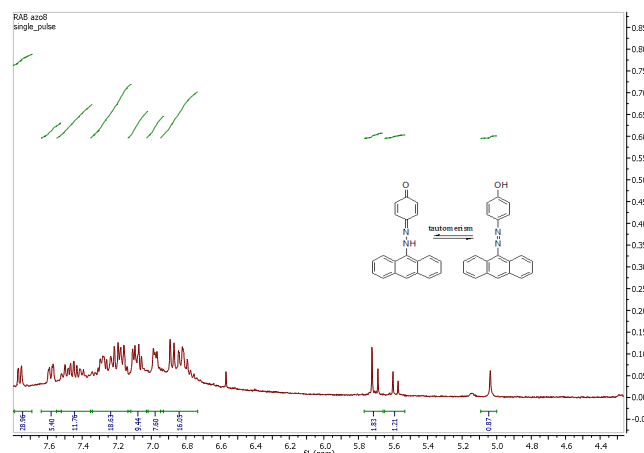


Fig. 3 The HNMR confirms the formation of the two tautomers 3 and 4

IV. CONCLUSION

Azo hydrazone tautomerism was proved to be taking place during the synthesis of 4-(9-anthrylazo) phenol **3** in which the other tautomer 4-[2-(anthracen-9-yl)hydrazono]cyclohexa-2,5-dienone **4** was also formed. These two tautomers were formed in ratio of (1:1).

ACKNOWLEDGMENTS

Authors would like to thank the chemistry department and the research centre at the Misurata University for facilitating the essential needs that were required for this project. .

REFERENCES

- [1] F. Van der Zee ; *Anaerobic Azo Dye Reduction*, 2002, Thesis Wageningen University, Wageningen, Netherlands, pp 2 – 7, 32, 33, 84.
- [2] H. Erkkut; *Biodegradation of Azo Dyes*, Springer-Verlag, Berlin Heidelberg, Germany, 2010, Vol. 9, pp 40 – 42.
- [3] M. Aziz and H. El-Mallah, “Electrical and optical properties of azo dye”, *Indian Journal of Pure and Applied Physics*, vol. 47, 2009, pp 530 - 534.
- [4] S. Yin, H. Xu, W. Shi, Y. Gao, Y. Song, J. Lam and B. Tang, “Synthesis and optical properties of polyacetylenes containing nonlinear optical chromophores”, *Polymer*, vol. 46, 2005, pp. 7670 – 7677.
- [5] A. Pielasz, “The process of the reduction of azo dyes used in dyeing textiles on the basis of infrared spectroscopy analysis”, *J. Mol. Struct.*, vol. 511-512, 1999, pp. 337 – 344.
- [6] N.A. Oranusi, C.J. Ogugbue, “Effect of pH and Nutrient Starvation on Biodegradation of Azo Dyes by *Pseudomonas*”, *J. Appl. Sci. Environ. Mgt.*, vol. 9, 2005, pp. 39 – 43.
- [7] G. Hallas, J.-H. Choi, “Synthesis and properties of novel aziridinyl azo dyes from 2-aminothiophenes—Part 2: Application of some disperse dyes to polyester fibers” *Dyes Pigm.*, vol. 40, 1999, pp. 119 – 129.
- [8] M.A. Weaver, L. Shuttleworth, “Heterocyclic diazo components”, *Dyes Pigm.*, vol. 3, 1982, pp. 81 – 121.
- [9] Y. Cheng, M. Zhang, H. Yang, F. Li, T. Yi, C. Huang, “Azo dyes based on 8-hydroxyquinoline benzoates: Synthesis and application as colorimetric Hg²⁺-selective chemosensors”, *Dyes Pigm.*, vol. 76, 2008, pp. 775 – 783.
- [10] P. Kaur, S. Kaur, A. Mahajan, K. Singh, “Highly selective colorimetric sensor for Zn²⁺ based on heterozylozo derivative”, *Inorg. Chem. Commun.*, vol. 11, 2008, pp. 626 – 629.
- [11] M.M.M. Raposo, M.C.R. Castro, M. Belsley, A.M.C. Fonseca, “Push-pull bithiophene azo-chromophores bearing thiazole and benzothiazole acceptor moieties: Synthesis and evaluation of their redox and nonlinear optical properties”, *Dyes Pigm.*, 2011, 91, 454 – 465.
- [12] A. S. Ozen, P. Doruker and V. Aviyente, “Effect of Cooperative Hydrogen Bonding in Azo-Hydrazone Tautomerism of Azo Dyes”, *J. Phys. Chem. A.*, vol. 111, 2007, pp. 13506 – 13514.
- [13] R. A. Bawa, E. M. Alzaraide and N. N. Ben Ehmidah, “Synthesis and electric conductivity study of the new azo dye 4-(9-anthrylazo)phenol”, *Int. Journal of Engineering Research and Application*, vol. 3, 2013, pp. 1 – 5.
- [14] I. Mohammed and A. Mustapha; “Synthesis of new azo compounds based on *N*-(4-hydroxyphenyl)maleimide and *N*-(4-methylphenyl)maleimide”, *Molecules*, vol. 15, 2010, pp. 7498 – 7508.
- [15] R. A. Bawa, E. J. Zaghloot, K. E. Mossa and N. O. Issa; “Synthesis and electric conductivity study of 4-(*p*-aminophenylazo) benzene sulphonic acid”, *Journal of Materials Science and Engineering B*, vol. 3, 2013, pp. 167 – 170.