

SYNTHESIS OF A NEW VAT DYE II

*¹Nwokonkwo D.C., ²Okafor C. O.

¹Department of Industrial Chemistry Faculty of Applied Physical Sciences,
Ebonyi State University Abakaliki.
(mirinkwa@gmail.com)

²Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria.

Abstract—A nitro dye of indigoid skeleton was synthesized by reaction of a nitro derivative of aniline: 2, 4-dinitroaniline and chloroacetic acid. The reaction was carried out in the presence of sodium hydroxide and high boiling solvent nitro benzene, under anhydrous conditions, maintained at an approximate temperature of 300°C. The product which was obtained and then used as the substrate for the nitro dye was purified by column chromatography using methanol and a suspension of activated carbon in distilled water. The intermediate produced from the reaction was in turn treated with an intimate mixture of sodium hydroxide- potassium hydroxide - sodamide in proportions of 5:5:1 ratio at a temperature not higher than 120°C; an intramolecular cyclization reaction yielded an indoxyl. Super concentrated aqueous solution of acidified Iron (III) chloride was used as an oxidant on this intermediate indoxyl. This reaction yielded the nitro dye which was a vat dye. The yield was excellent and the structure of this compound was established as tetranitroindigo by chemical evidence: ultraviolet, infrared, nuclear magnetic resonance spectroscopy and mass spectrometry. The indoxyl was reduced with sodium hydrosulphite (Na₂S₂O₄) and was easily oxidized by air to the nitro dye, one of the characteristics of vat dyes.

Keywords: Nitroaniline, Chemical evidence, nitro dye, Reduction. Synthesis, Vat dye

1 INTRODUCTION

Dyes and dye intermediates are used as indicators or in colouring foods, drugs, cosmetics, textiles, plastics, solvents, waxes, papers etc [1], [2], [3], [4], [5], [6], [7], [8], [9]. Indigo compounds are important compounds that are useful as dyes [10], [11]. The presently employed industrial processes for the preparation of indigo comprised forming an N-phenylglycine salt from aniline or any other suitable derivative of aniline or a heterocyclic ring having nitrogen as a hetero atom and chloroacetic acid, then converting this salt into an indoxyl compound by alkali fusion at elevated temperature, and then oxidizing this compound in air [12], [13], [14], [15], [16], [17], [18], [19]. In this article, indigo dye, a vat dye was prepared by using 2, 4- dinitroaniline, chloroacetic acid to give an intermediate 2, 4- dinitrophenylglycine. This was fused with sodium hydroxide, potassium hydroxide and sodamide at a temperature between 110-120°C to give an indoxyl. This indoxyl was oxidized using acidified solution of Ferric chloride to form a blue vat dye [20], [21].

2 Material and Methods

All reagents were of analytical grade, melting point was taken on Gallenkamp melting point apparatus in open capillaries and are reported uncorrected. Infrared was performed on Perkin Elmer Model 337 from Central Research Laboratory University of Ibadan, Nigeria using potassium bromide discs and also dimethylsulphoxide was used where applicable. The ultraviolet-visible spectra were recorded on UVI spectrophotometer Model 061408 using 1cm quartz cells. The solvent used were deuterated water, distilled water and dimethylsulphoxide at Central Science Laboratory Obafemi Awolowo University Ile-Ife Nigeria. ¹H- and ¹³C were determined on FT model 65336 in deuterated dimethylsulphoxide using trimethylsilane as internal standard at ambient temperature. The chemical shifts were reported on the δ scale at Central Science Laboratory Obafemi Awolowo University Ile-Ife Nigeria.

The mass Spectra were obtained on an AEIMS9 double focusing mass spectrometer at 70Ev at Usman Danfodio University Nigeria.

2.1 Synthesis of the Intermediate: 2, 4-Dinitrophenylglycine

About 20g (0.11 mol) of 2, 4-Dinitroaniline was introduced into a 500 mL round bottomed flask, to this were added 30g (0.32 mol) of chloroacetic acid and 20 g (0.5mol).sodium hydroxide. To this mixture was introduced 50mL of nitrobenzene and refluxed for six hr at a temperature of approximately 300°C. A progressive colour change from yellow, red to black as heating continued was observed. The slurry that formed was allowed to cool and washed with methanol (4 x 200 mL). The crude product that was obtained, was a milky amorphous powder. This compound was soluble in water but insoluble in organic solvents like acetone. It was then dissolved in water, treated with activated carbon and filtered. A 20.4 g dirty white powder was obtained after distilling off the solvent.

The melting point was 185-186°C. The UV: (EtOH) (nm) λ min 345, λ max 355, IR: (cm⁻¹) 3380 (d, NH), 3100 (s, OH, carboxylic), 1720 (s, C=O, carboxylic overtone) 1610-1420(C-H, arom.), 1300(s, NO₂). ¹H-: (CDCl₃) δ : 4.0 (d, NH), 4.0 (t, CH₂) 6.95 (1H, d, =CH, arom), 8.36 (1H, d, =CH, arom.), 8.36 (1H,d), 8.90 (1H,s), 11.0 (1H, s, COOH). ¹³C: (CDCl₃) δ :45.0(CH₂),115.3(C- 5,arom),119 (C-2,arom) , 128.0 (C-4,arom), 133.1 (C-1, arom.), 137.7 (C-3,arom.), 144.7 (C-6,arom),173.2 (COOH). MS m/e: 242.03 (1.1, M++H) 243.04(1.6, M++2H), 242.04 (9.0, M++H), 241.03 (M+, 100). Analytical calculation for M m/e C₈H₇N₃O₆: C, 39.84,

O, 39.81. Found C, 39.67, H, 2.83, N, 17.62, O, 39.71.

The suggested reactions involved and the intermediate structure are shown in Scheme 1.

2.2 Synthesis of 4, 4', 7, 7'-tetranitroindigo dye from 2, 4-dinitrophenylglycine

Approximately 6.0 g (0.025 mol) of 2,4-dinitrophenylglycine; 30.0 g (0.75 mol) of sodium hydroxide; 30.0 g, (0.54 mol) of potassium hydroxide and 6.0 g (0.15 mol) of sodamide were ground intimately in a mortar and introduced into a 250 mL pyrex conical flask. The mixture was moistened with 50 mL nitrobenzene, corked and heated slowly for 90 min. The colour change progressed from yellow to deep yellow and finally red-orange. As the temperature increased, the mixture became a liquid and finally solidified. The fused mixture was allowed to cool and dissolved in cold water; the solution was agitated for 1 hr and then treated with 100 mL solution of FeCl₃ acidified with 50 mL of concentrated HCl to facilitate precipitation or oxidation of the dye. The blue dye that formed was recrystallized from acetone and dried. The melting point was > 390°C. The UV (λ_{max} nm)(DMSO) 720 (ϵ 1270), IR (cm⁻¹): 3130 (ring NH), 1320 (N=O), 1450 (aromatic), 1680-1750 (C=O), 1310-1295 (s,C=C), ¹H- (CDCl₃) δ : 4.0 s (1,11- NH), 8.88 s (4,41-1H) 9.15 s (6,61-1H), ¹³C- (CDCl₃) δ : 114.3 (2 C, arom, 3°), 125.3 (2=CH), 127.7 (2 C, arom, 3°), 131.7(2 C, arom, 2°), 136.4 (2C, arom), 139.8 (2C, arom, 3°), 149.1 (2C, arom, 3°), 187.0 (2 C=O). The suggested reaction pathways and structures are shown in Scheme 2.

2.3 Reduction of the dye

about 50 mL dimethylsulphoxide (DMSO) solution of 1.0g dye was added four molar equivalents of sodium hydrosulphite(Na₂S₂O₄) and the mixture heated under reflux for 2 hr, during which time the dye lost its colour as it was reduced to the dihydro derivative- leuco. The solution was poured into an iced cold solution of sodium hydrosulphite in 150 mL of water, the slurry was stirred and filtered. In the process, the reduced dye was re-oxidized to the original starting dye resulting in the regeneration of the original colour and isolation of a product which was characterized as the starting material.

3 Results

A blue compound of indigoid structure was prepared using 2, 4-dinitroaniline for the first time. This was treated with chloroacetic acid under alkaline condition in the usual and already established Heumann reaction pathway. An intermediate, 2, 4-dinitrophenylglycine was obtained the melting point was 185-186°C. The intermediate product was treated with finely ground sodium hydroxide, heated at a temperature not exceeding 120°C, a blue compound was isolated after work-up. The choice of using acidified solution of ferric chloride to facilitate oxidation appeared most convenient and attractive [22], [23]. Elemental analysis and mass spectroscopy were in agreement with the molecular formula C₁₆H₆N₆O₁₀.

A band at 720nm characteristic of indigoid system was observed in the UV spectrum. The infrared spectrum showed a sharp band at 3130 cm⁻¹ due to the presence of secondary aromatic NH group [24], [25], also there were significant bands at 1680-1750cm⁻¹. Further evidence of structure was provided by the ¹H and ¹³C NMR. MS m/e 442.01 (100%, M⁺), 443.02 (17.8%, M⁺+H), 443.01(2.2% M⁺+H), 444.02 (3.5% M⁺+2H). C, 43.45, H, 1.37, N, 19.00 and O, 36.18. The fastness of this compound to light, acid, base, organic solvents gave excellent results.

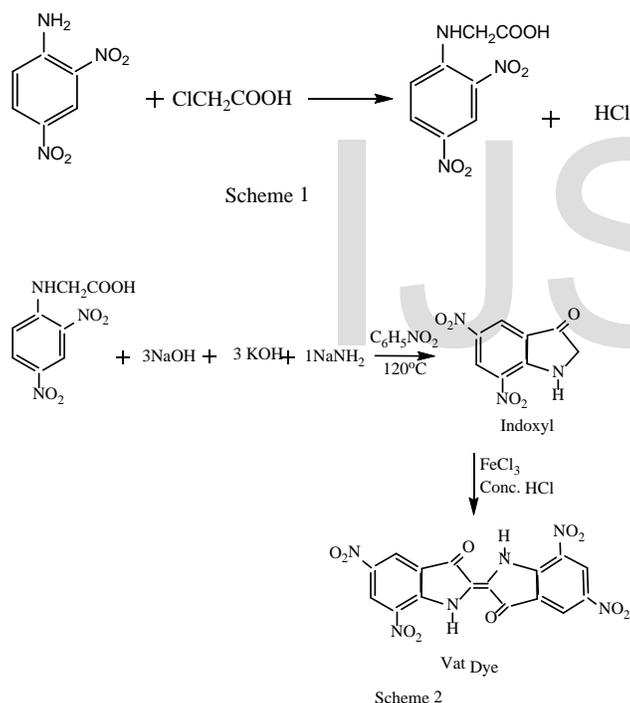
4 Discussion

The substitution nucleophilic bimolecular reaction, with chloroacetic acid reagent and 2, 4- dinitroaniline as the nucleophile under basic condition, yielded a milky powder of molecular weight C₈H₇N₃O₆ melting at 185- 186°C. The molecular ion appeared in the mass spectrum at m/e 241.03, molecular formula C₈H₇N₃O₆. The ultraviolet spectrum showed two maximum absorption bands at 345nm and 355 nm. The infrared spectrum had strong bands at 3380 cm⁻¹ (d, NH, arom) for 2° NH stretch, 3650 cm⁻¹ (b, OH) for O-H stretch of carboxylic acids, 1720 cm⁻¹ (s, CO) stretch of carboxylic acid, 1340 cm⁻¹ (s, NO₂) stretch for aromatic C-NO₂ and 1600-1300 cm⁻¹ (=CH, arom) characteristic aromatic vibrations. ¹H- chemical shift at 4.0 δ (s, 1H) showed NH proton, 4.0 δ (s, 2H) for CH₂, 6.95 δ and 8.36 δ (d, 1H) methine protons –aromatic, 8.90 δ (s, 1H) methine proton, aromatic and 11.0 δ (s, 1H) for carboxylic acid. ¹³C- chemical shifts appeared at 128.0 (C5), 133.1 (C2), 137.7 (C4), 144.7 (C1), 119.5 (C3) and 115.3 (C6) these were methine carbons of benzene. The molecular peak was found at m/e 241.03(M⁺, 100%) the parent ion which corresponded to molecular formula C₁₆H₆N₆O₁₀. This compound was given the name 2, 4-dinitrophenylglycine. This compound under fusion with admixture NaNH₂: KOH: NaOH (1:5:5) at a moderate temperature of 120°C gave a blue compound. The melting point was above 390°C and the compound was soluble in dimethylsulphoxide, dimethylformamide and concentrated sulphuric acid: the same solubility properties as indigo. The Ultraviolet absorption maximum at 720 nm in DMSO was indicative of indigoid structure. The strong bands at 3280 cm⁻¹ (m, NH, arom) for 2° NH stretch, 1725 cm⁻¹ (s, CO) stretch of ketones 1340 cm⁻¹ (s, NO₂) stretch for aromatic C-NO₂, 1620cm⁻¹ (C=CH, arom, conjugated), 1570-1440 cm⁻¹(CH, arom) characteristic aromatic vibrations are characteristic vibrations. ¹H- chemical shift at 4.0 δ (s, 1H) showed NH proton, 4.0 δ (s, 2H) for CH₂, 6.95 δ and 8.36 δ (d, 1H) methine protons – aromatic, 8.90 δ (s, 1H) methine protons aromatic and 11.0 δ (s, 1H) for carboxylic acid. The absence of absorption band at 3650 cm⁻¹ confirmed the lost or absence of hydroxyl group of carboxylic acids (COOH) while the band at 1725 cm⁻¹ was for ketones, 1620 cm⁻¹ stretch showed the presence of conjugated C=C of aromatic compound. The ¹H- showed three peaks at 4.0 δ (s, 2NH), 8.88 δ (s, 2CH)

and 9.15 δ (s, CH-NO₂). ¹³C- chemical shifts appeared at δ 127.7 (q, 2C=C), δ 187.0 (2C=O), δ 114.03 (q, 2C), δ 131.7 (d, 2=CH), δ 139.8 (2C-NO₂), δ 125.3 (d, 2=CH), δ 136.4 (q, C-NO₂) and 149.1 (q, 2=CH) these were methine carbon of benzene and carbonyl shifts. The molecular peak was found at m/e 442.01 (M+, 100%), the parent ion which corresponded to molecular formula C₁₆H₆N₆O₁₀: C, 43.45, H, 1.37, N, 19.00 and O, 36.18. From the proposed structural evidence, the compound was given the nomenclature 5, 5', 7, 7'-tetranitroindigo.

Conclusion

5, 5', 7, 7'-tetranitroindigo was a new indigo dye as suggested by and evidenced from the IR, UV and Mass spectrometry carried out. The chemical properties, physical properties as well as the dyeing properties were similar to those of commercial indigo dye in the market/circulation.



References

- [1] D.A. Skoog, D.M. West, F.J Holler and S.R.Crouch (2004). Fundamentals of Analytical Chemistry 8th Ed. Saunders College, USA, pp. 335-625.
- [2] D. Del Pozo-Insfran, C.H. Brenes and S.T.Talcott (2004). Phytochemical Composition and Pigment Stability of Acai, *J. Agric Food Chem.* vol.52, no.6, pp.1539- 45.
- [3] J.E. Ekandem and A.U. Owor (1997). Local Flower Extracts as Simple Acid-Base Indicators. *J.Chem.Soc.,Nig.*, vol. 22, pp. 98-103.
- [4] M.E. Soltan and S.M. Sirry (2002). Usefulness of Some Plant Flowers as Natural Acid-Base Indicators, *J. Chinese Chem. Soc.*, vol.49, pp.631-652.
- [5] D. Graham (1972). Colour and Chemical Constituents of Dyes in Lubs H.A ed. The Chemistry of Synthetic Dyes and Pigments, Am. Chem Soc., Monograph Series, Krieger Pub.Co. New York, p.581.
- [6] M.U. Akpuaka C. Chukwunke and G. Agbo (1998). *J.Chem.Soc. Nig.* vol. 23, p.47.
- [7] K. Othmer (1965). Encyclopaedia of Chem. Tech. 2nd .Ed, Interscience New York, 462.
- [8] Thorpe J.F. and Whitely M.A., (1940). Thorpe's Dictionary of Applied Chemistry, 4th.Ed. Longman's London, 121.
- [9] E. R.Trotman (1970). Dyeing and Chemical Technology of Textile Fibers, Charles Griffin and Co.Ltd.London, 305.
- [10] A.L. Serrano and B.O.Roos (1996). The Theoretical Study of Indigoid Dyes and Their Chromophore, *Eur J. Chem.* vol. 3, no.5, pp. 717-725.
- [11] Baeyer, A. (1878). Ber., 1296.
- [12] Baeyer, A. (1879). Ber., 456.
- [13] Sachs F. and R. Kempf (1903). Ber., Dtsch. Chem. Ges, 36.
- [14] Posner T. (1903). Ber., Dtsch.Chem. vol.59, pp.1799-1833.
- [15] I. Shingo (2002). *J. Photochem and Photobio. Chem.* 149 (1-3), 121-130.
- [16] C. Kos (1997). Process for the Preparation of Indigo U.S. Patent 5, 686,625
- [17] Y. Yamamoto, U. Takaki, S. Aoki and I.Hara (1990). Process for The preparation of Indigo U.S. Patent 4,706-973.
- [18] K. Heumann (1890). Ber., 23, 3043.
- [19] B.T. Golding and C. Pierpont (1986). Indigo Blue, Educ. Chem., pp.71-73.
- [20] W.A. Smith, A. Floods, D. Bochkov and R. Caple (2006). Organic Synthesis, *Royal Soc. Chemists*, 4.
- [21] J.O. Otutu, D.O. Ukponmwan and A.P.Oviawe (2007). Synthesis and Fastness Properties of Diazo Dispers Dyes from 4- Aminophenol, *J. Chem. Soc. Nig.*, vol.32 no.2, pp.65-71.
- [22] B.R., Sharma (2006). Industrial Chemistry including Chemica Engineering, 15th.Ed. Geol.Pub.House Meerut, 1548.
- [23] C.O.Okafor (1980). Studies in Heterocyclic Series XVII, *J.Het. Chem.* 17, 149.
- [24] C.O. Okafor, (1975). Heterocyclic Series X. *J. Org. Chem.* 40, 2753
- [25] I. L.Finar (1973). Organic Chemistry, I, Longman, London,