

## Synthesis of a New Indigo Vat Dye

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### Abstract

A new blue indigo vat dye was prepared from 2, 4-dinitroaniline. 2, 4 dinitroaniline was used as the nucleophile and treated with chloroacetic acid which was the substrate-the alkylhalide. The reaction was a base catalyzed substitution nucleophilic bimolecular (S<sub>N</sub>2) reaction using nitrobenzene as solvent because it had high boiling point. The reaction was carried out at an elevated temperature of 300°C. An intermediate compound was formed, isolated and purified. This isolated compound was treated with an intimate mixture of sodamide, sodium hydroxide and potassium hydroxide in the 1:5:5 ratios at a temperature above 100°C. An orange-red compound which resulted from this intramolecular cyclization reaction was dissolved in 200 mL of purified water and filtered. The solution was treated with 150 mL concentrated acidified solution of Ferric Chloride to give a dark blue compound. The structure of this compound by chemical evidence: Ultraviolet, Infrared, Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry was established as 5, 5<sup>1</sup> 7, 7<sup>1</sup> -tetranitroindigo. This compound was reduced with sodium dithionite (sodium hydrosulphite) to the leuco or colourless form which was insoluble in water and was oxidized by air readily to the original blue compound, one of the characteristics of vat dyes.

**Keywords:** Dinitroaniline, Chemical evidence, Indigo dye, Reduction. Synthesis, Vat dye

### Introduction

Dyes and pigments belong to important group of compounds used to impart the desired colours to bodies on which they are applied. They may impart these colours by adhesion to the surface of the substance or by interaction with the chemical

components of the substance. Therefore dyes and dye intermediates are used as indicators or in colouring foods, drugs, cosmetics, textiles, plastics, solvents, waxes, papers etc <sup>[1-9]</sup>. Indigo compounds are important compounds that are useful as dyes <sup>[10-11]</sup>, indigo dye was obtained both from dyer's woad indigenous in Europe and from "Indigofera tinctoria", a native plant of Asia. The presently employed industrial processes for the preparation of indigo comprise forming an N-phenylglycine salt from aniline and chloroacetic acid, converting this salt into an indoxyl compound by alkali fusion at elevated temperature, and then oxidizing this compound with air <sup>[12-19]</sup>. The importance of vat dyes especially those derived from indigo and its derivatives is still relevant and prompted this investigation. In this article, indigo dye, a vat dye was prepared by using 2, 4-dinitroaniline, chloroacetic acid in the presence of a base 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 treated with concentrated acidified solution of Ferric Chloride to yield a blue vat dye <sup>[20-21]</sup>.

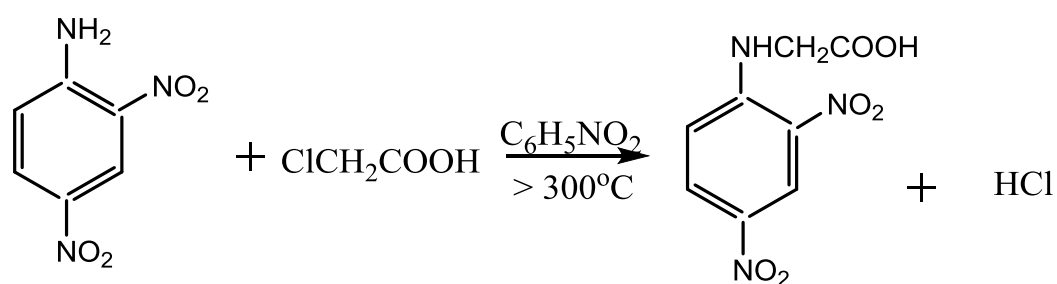
## Material and Material and Methods

All reagents that were used were of analytical grade, melting point was taken on Gallenkamp melting point instrument in open capillaries and were reported uncorrected. <sup>1</sup>H- and <sup>13</sup>C were determined on FT model 65336 in deuterated dimethylsulphoxide using trimethylsilane as internal standard at ambient temperature and the chemical shifts were reported on the  $\delta$  scale, while Infrared was performed on Perkin-Elmer Model 337 using potassium bromide discs and dimethylsulphoxide was used where applicable at Central Research Laboratory University of Ibadan, Nigeria. The ultraviolet-visible spectra were recorded on UVI spectrophotometer Model 061408 using 1cm quartz cells; the solvents used were deuterated water, distilled water and dimethylsulphoxide at Central Science Laboratory Obafemi Awolowo University Ile-Ife Nigeria. The mass Spectra were obtained on an AEIMS9 double focusing mass spectrometer at 70Ev, this analysis was carried out at Usman Danfodio University Sokoto Nigeria.

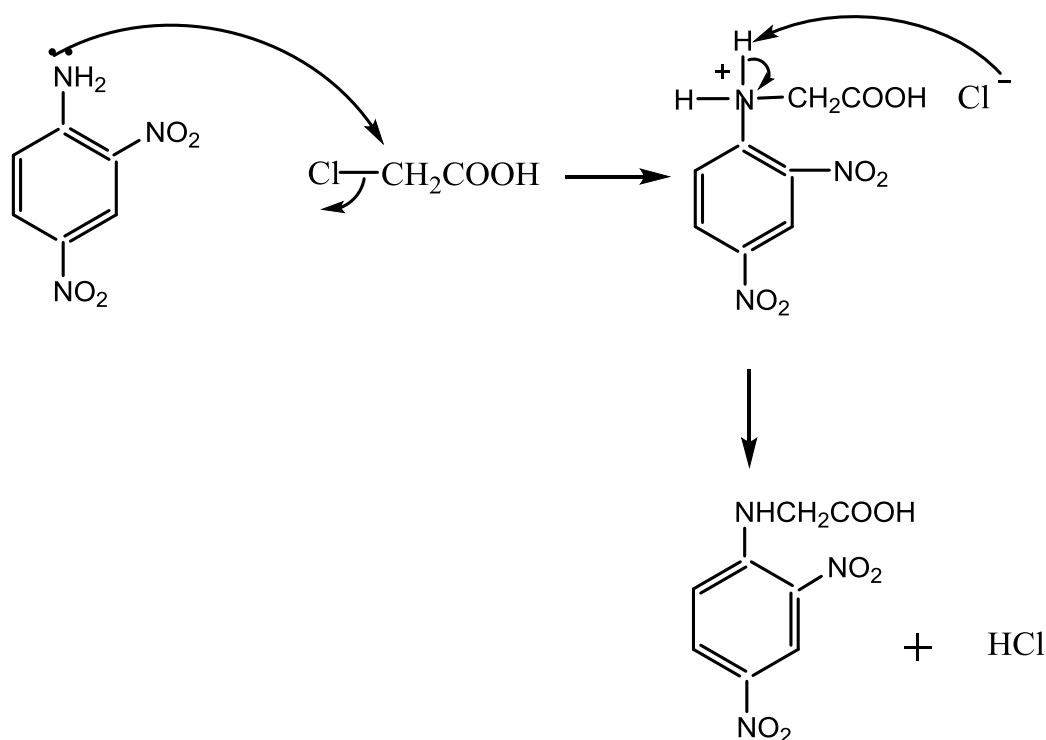
### Synthesis of the Intermediate: 2, 4-Dinitrophenylglycine

About 20 g of 2, 4-dinitroaniline (0.11 mol), 30 g chloroacetic acid (0.32 mol), 20 g sodium hydroxide (0.5 mol) and 50 ml of nitrobenzene were introduced into a 500 ml round bottomed flask, and refluxed for six hrs at a temperature of approximately 300°C on magnetic stirrer heater. As refluxing progressed, the colour progressively changed from the predominantly yellow colour of 2, 4-dinitroaniline to red and finally to dark colour. The mixture was allowed to cool and washed with small portions of 800 ml methanol. The crude product that was obtained was a milky amorphous powder. This compound dissolved in water but not in organic solvents like acetone. An aqueous solution of the compound was treated with activated charcoal and filtered. About 20.4 g of pure white powder crystallized after distillation. The melting point was 185-186°C. The UV spectra measured in nanometers using ethanol showed absorptions at  $\lambda$  min 345,  $\lambda$  max 355; IR spectra in  $\text{cm}^{-1}$  showed absorptions at 3380

(d, NH), 3100 (s, OH, carboxylic), 1720 (s, C=O, carboxylic overtone) 1610-1420(C-H, arom. ), 1300(s, NO<sub>2</sub>). <sup>1</sup>H-NMR in deuterated chloroform on the delta scale showed signals at δ 4. 0 (d, NH), δ 4. 0 (t, CH<sub>2</sub>) δ 6. 95 (1H, d, =CH, arom), δ 8. 36 (1H, d, =CH, arom. ), δ 8. 36 (1H, d), δ 8. 90 (1H, s) and δ 11. 0 (1h, s, COOH). <sup>13</sup>C-NMR in deuterated chloroform exhibited signals at δ 45. 0(CH<sub>2</sub>), δ 115. 3(C-5, arom), δ 119 (C-2, arom), δ 128. 0 (C-4, arom), δ 133. 1 (C-1, arom. ), δ 137. 7 (C-3, arom. ), δ 144. 7 (C-6, arom) and δ 173. 2 (COOH). MS showed peaks at m/e: 242. 03 (1. 1, M++H), 243. 04(1. 6, M++2H), 242. 04(9. 0, M++H) and 241. 03 (M+, 100). Analytical calculation for m m/e C<sub>8</sub>H<sub>7</sub>N<sub>3</sub>O<sub>6</sub>: C, 39. 84, H, 2. 93, N, 17. 42, O, 39. 81. Found C, 39. 67, H, 2. 83, N, 17. 62, O, 39. 71. the probable reactions involved and the intermediate structure were shown in scheme 1.



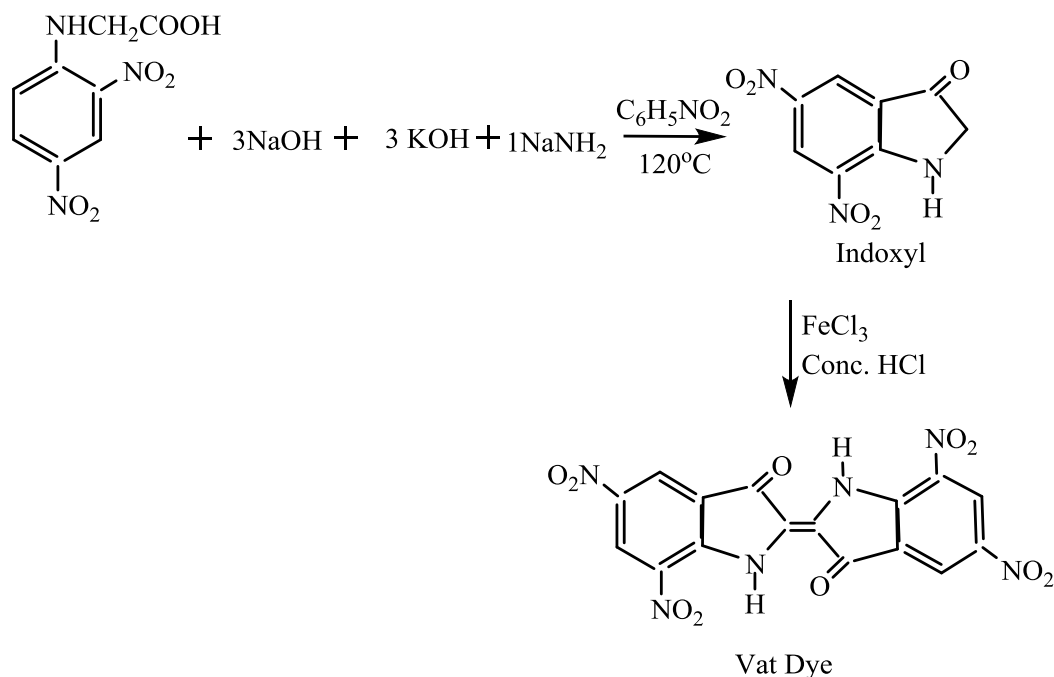
Mechanism of Reaction



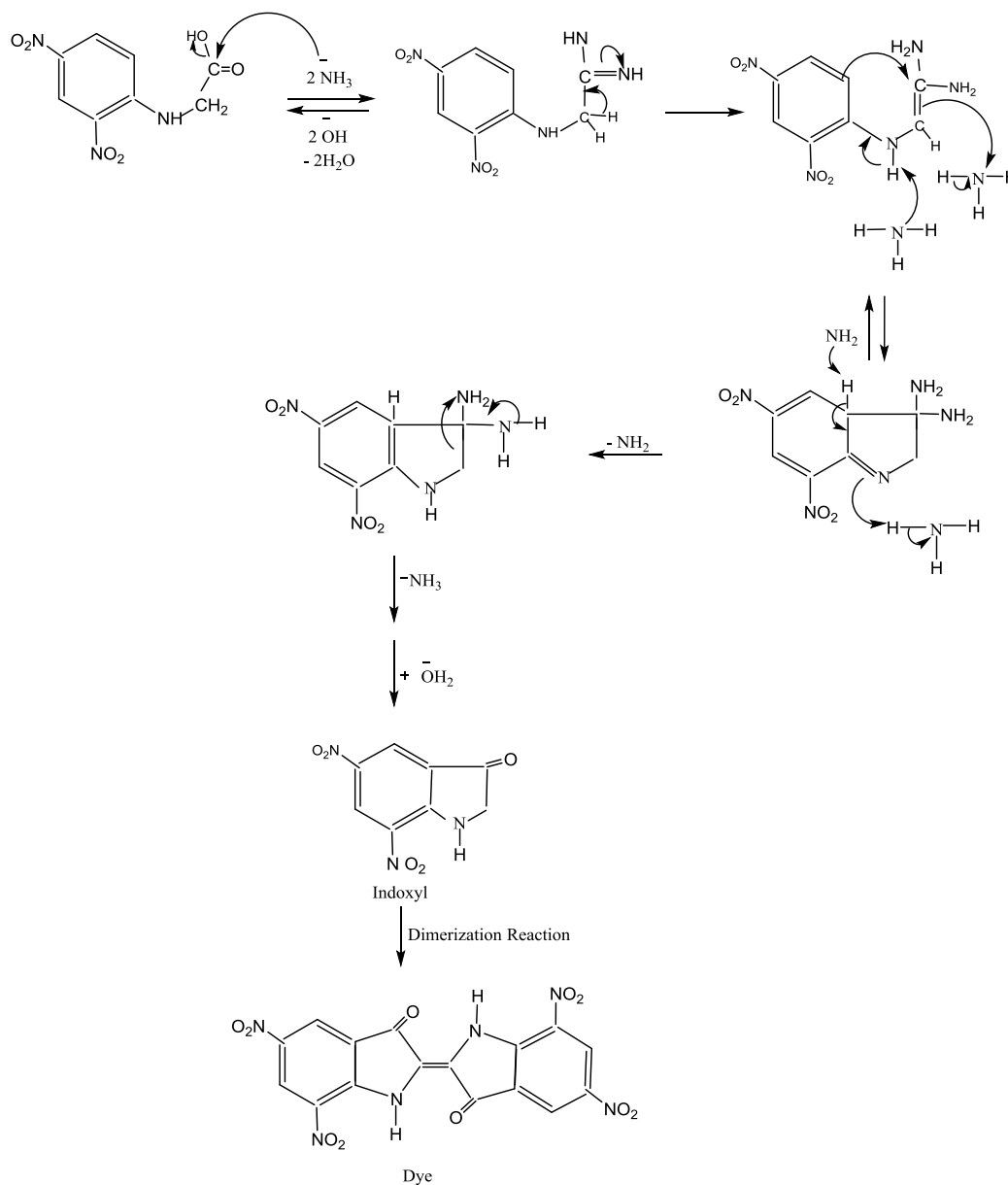
Scheme 1

### Synthesis of 5, 5<sup>1</sup>, 7, 7<sup>1</sup> -Tetranitroindigo dye from 2, 4-Dinitrophenylglycine:

Approximately 6.0 g of 2, 4-dinitrophenylglycine (0.025 mol), 30.0 g of sodium hydroxide (0.75 mol), 30.0 g potassium hydroxide (0.54 mol) and 6.0 g, sodamide (0.15 mol) were ground together in a porcelain mortar and introduced into a 250 mL quick fit conical flask. To this mixture was added 40 mL nitrobenzene, corked and heated slowly for 90 min. The colour change from colourless, yellow, deep yellow and finally to red-orange was prominent. The mixture melted gradually, became molten and solidified as the reaction temperature increased. The fused mixture was allowed to cool and dissolved in cold water; the solution was stirred for 1 hr and then treated with 100 mL of 3 M FeCl<sub>3</sub> solution acidified with concentrated HCl (50 mL) 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 spectra measured in nanometers using dimethylsulphoxide showed an absorption at 720 (ε 1270), IR spectra in cm<sup>-1</sup> showed absorptions at 3130 (ring NH), 1320 (N=O), 1450 (aromatic), 1680-1750 (C=O), 1310-1295 (s, C=C), <sup>1</sup>H-NMR in deuterated chloroform on the delta scale showed signals at δ 4.0 s (1, 11-NH), δ 8.88 s (4, 41-1H) and δ 9.15 s (6, 61-1H), <sup>13</sup>C-NMR in deuterated chloroform exhibited signals at δ 114.3 (2 C, arom, 3°), δ 125.3 (2=CH), δ 127.7 (2 C, arom, 3°), δ 131.7 (2 C, arom, 2°), δ 136.4 (2C, arom), δ 139.8 (2C, arom, 3°), δ 149.1 (2C, arom, 3°) and δ 187.0 (2 C=O). The suggested reaction pathways and structures are shown in Scheme 2.



Mechanism of Reaction



Scheme 2

**Reduction of the dye:**

About 50 mL dimethylsulphoxide (DMSO) solution of the 1.0 g dye was added four molar equivalents of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) and the mixture heated under reflux for 2 hr, the blue colour of the dye disappeared as the dye was reduced to the leuco colourless form or the dihydro derivative. The solution was poured into an iced cold solution of sodium hydrosulphite in 150 mL of water; the slurry was stirred and

filtered. As stirring progressed, 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.

## Results

A blue vat dye was prepared using 2, 4-dinitroaniline probably for the first time. 2, 4-dinitroaniline was treated with chloroacetic acid under basic condition using the already established Heumann reaction method. An intermediate, 2, 4-dinitrophenylglycine was obtained with a melting point of 185-186°C and molecular weight  $C_8H_7N_3O_6$ . This intermediate product was used as a precursor in the second reaction by reacting it with admixture of sodium hydroxide, potassium hydroxide and sodamide under anhydrous condition. The solid mixture was heated at an average temperature range of 120°C; a dark-blue compound was isolated after filtration, solvent extraction and chromatography. The choice of using concentrated acidified solution of Ferric chloride to facilitate oxidation was invented by the author since this method precipitated the dye under five min. [22-23]. Elemental analysis and mass spectroscopy were in agreement with the molecular formula  $C_{16}H_6N_6O_{10}$ . A band at 720 nm characteristic of indigoid system was observed in the UV spectrum. The infrared spectrum showed a sharp band at  $3130\text{ cm}^{-1}$  due to the presence of secondary aromatic NH group [24-25], also there were significant bands at  $1680\text{-}1750\text{ cm}^{-1}$ . Further evidence of structure was provided by the  $^1\text{H}$  and  $^{13}\text{C}$  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. This compound was fast to light, acid, base and organic solvents and the results were excellent.

## Discussion

The reaction of chloroacetic acid as the substrate and 2, 4-Dinitroaniline as the nucleophile in a substitution nucleophilic bimolecular reaction under basic condition, yielded a milky powder of molecular weight  $C_8H_7N_3O_6$  with a melting point of 185-186°C. The peak at m/e 241. 03 was the molecular ion consistent with the molecular formula  $C_8H_7N_3O_6$ . The ultraviolet spectrum showed two maximum absorption bands at 345nm and 355 nm. The infrared spectrum had strong bands at  $3380\text{ cm}^{-1}$  (d, NH, arom) for  $2^\circ$  NH stretch,  $3650\text{ cm}^{-1}$  (b, OH) for O-H stretch of carboxylic acids,  $1720\text{ cm}^{-1}$  (s, CO) stretch of carboxylic acid,  $1340\text{ cm}^{-1}$  (s,  $\text{NO}_2$ ) stretch for aromatic C- $\text{NO}_2$  and  $1600\text{-}1300\text{ cm}^{-1}$  (=CH, arom) characteristic aromatic vibrations.  $^1\text{H}$ -chemical shift at  $4.0\delta$  (s, 1H) showed NH proton,  $4.0\delta$  (s, 2H) for  $\text{CH}_2$ ,  $6.95\delta$  and  $8.36\delta$  (d, 1H) methine protons -aromatic,  $8.90\delta$  (s, 1H) methine proton, aromatic and  $11.0\delta$  (s, 1H) for carboxylic acid.  $^{13}\text{C}$ -chemical shifts appeared at 128. 0 (C-5), 133. 1 (C-2), 137. 7 (C-4), 144. 7 (C-1), 119. 5 (C-3) and 115. 3 (C-6) these were methine carbons of benzene. The molecular peak was found at m/e 241. 03(M+, 100%) the parent ion which was consistent with the molecular formula  $C_{16}H_6N_6O_{10}$ ; this compound was given the name 2, 4-Dinitrophenylglycine [21]. 2, 4-Dinitrophenylglycine was in turn fused with admixture  $\text{NaNH}_2$ :  $\text{KOH}$ :  $\text{NaOH}$  (1:5:5)

at a moderate temperature of 120°C and gave a dark-blue compound. The melting point was above 390°C and the compound was soluble in dimethylsulphoxide (DMSO), dimethylformamide (DMF) and concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>): the same solubility properties as indigo. The Ultraviolet absorption maximum at 720 nm in DMSO was indicative of indigoid structure also. The strong bands at 3280 cm<sup>-1</sup> (m, NH, arom ) was for 2° NH stretch, 1725 cm<sup>-1</sup> (s, CO ) was stretch of ketones, 1340 cm<sup>-1</sup> (s, NO<sub>2</sub>) stretch for aromatic C-NO<sub>2</sub>, 1620 cm<sup>-1</sup> ( C=CH, arom, conjugated ) and 1570-1440 cm<sup>-1</sup>( CH, arom) which were characteristic of aromatic vibrations. <sup>1</sup>H-chemical shift at 4. 0 δ (s, 1H) showed NH proton, 4. 0 δ (s, 2H) for CH<sub>2</sub>, 6. 95 δ and 8. 36 δ (d, 1H) methine protons – aromatic, 8. 90 δ (s, 1H) aromatic methine proton and 11. 0 δ (s, 1H) for carboxylic acid. The absence of absorption band at 3650 cm<sup>-1</sup> confirmed the lost or absence of hydroxyl group of carboxylic acids (COOH) while the band at 1725 cm<sup>-1</sup> was for ketones, 1620 cm<sup>-1</sup> stretch showed the presence of conjugated C=C of aromatic compound. The <sup>1</sup>H-showed three peaks at δ 4. 0 (s, 2NH), δ 8. 88 (s, 2CH) and δ 9. 15 (s, CH-NO<sub>2</sub>). <sup>13</sup>C-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-NO<sub>2</sub>), δ 125. 3 (d, 2=CH), δ 136. 4 (q, C-NO<sub>2</sub>) and 149. 1 (q, 2=CH) these were significant shifts for methine carbon atoms of an aromatic system and characteristic carbonyl shifts. The molecular peak was found at m/e 442. 01(M<sup>+</sup>, 100%), the parent ion which corresponded to molecular formula C<sub>16</sub>H<sub>6</sub>N<sub>6</sub>O<sub>10</sub>: 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<sup>1</sup>, 7, 7<sup>1</sup> -Tetranitroindigo.

## Conclusion

The synthesis of this vat dye was probably the first of its kind as suggested and evidenced by the instrumental analyses: IR, UV, NMR and Mass Spectrometry carried out. The chemical properties, physical properties as well as the dyeing properties were similar to those of parent commercial indigo dye.

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