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Synthesis of Dye from Anthranilic Acid and Its Utility

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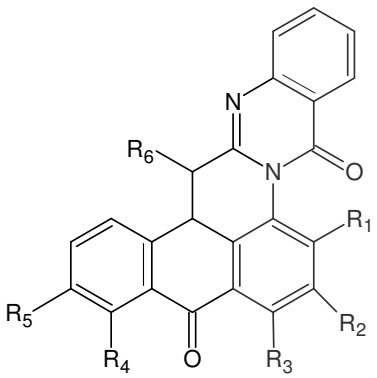
A new dye was synthesized from anthranilic acid by conversion of *p*-amino benzoic acid to HCl salt of ammonium benzoyl chloride. Condensation of HCl salt of ammonium benzoyl chloride with anthranilic acid at various conditions *viz.*, temperature, condition of reactant and solvents were maintained for the preparation of dye. The prepared dye was characterized on the basis of spectral data (IR, NMR and UV) and screened as an indicator in titrimetric analysis. This dye can be used as an indicator in both conditions when acid was titrate, base was titrant and *vice-versa*.

Key Words: Anthranilic acid, Thionyl chloride, *p*-Aminobenzoic acid, Pyridine.

INTRODUCTION

Colours are playing a dominant role in life of man from ancient time immemorial. Today colourants are used in information storage devices, lasers, liquid crystal displays, solar energy conversion system and as a food additive. Moreover analytical techniques such as affinity chromatography and histological techniques depend on dye[1].

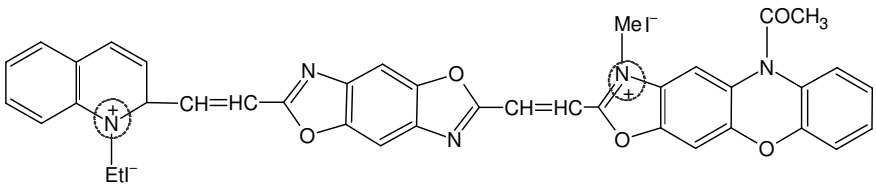
Lesser and Gad in 1930, patented a method for the preparation of naphtha [1′,2′,3′:4-5]-[2,1-b]quinazoline-5,10-dione by the reaction of 1-acetamidoanthraquinone with anthranilic acid in the presence of acetic anhydride and zinc chloride. This is found to be useful as a commercial disperse dyestuff for polyester fibre[2].



where R_1, R_2, R_3, R_4, R_5 = H

(**I**)

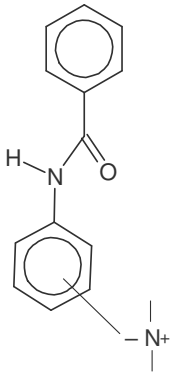
Styryl cyanine dyes find extensive application as photosensitizers for silver halide emulsions, textile dyes and as bactericidal agents[3].



(**II**)

Anthranilic acid is also well known dye intermediate. If we examine structure of dyes reported in literature survey have common -NHCO group which is flanked between two phenyl groups (I) and (II) possesses $-\overset{|}{\underset{|}{N}}+$ moiety contributing as chromophore.

From this assumption we can draw structure of lead molecule for colouration of dye given as below:

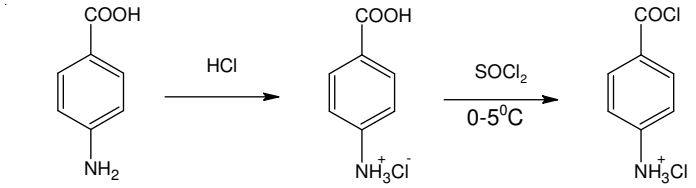


Anthranilic acid is a major dye intermediate physiologically, it is aromatic amine as a metabolite of tryptophan, as essential amino acid and industrially used as an intermediate in dye synthesis[4,5]. It was observed that this synthesized dye has a great potential value in acid base titration and *vice-versa* as an indicator.

EXPERIMENTAL

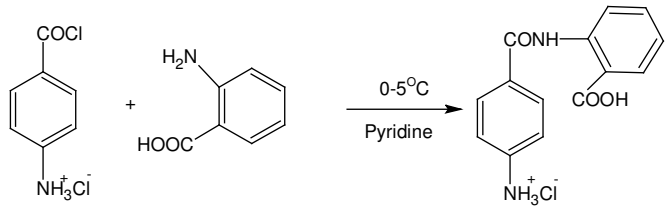
All the reagents and solvents used were of laboratory grade. The melting point of dye was determined by open capillary method and was uncorrected. The purity and homogeneity of compound was checked using TLC technique. The ultraviolet absorptions spectrum was measured in N,N-dimethyl formamide on Shimadzu 1601 spectrophotometer. IR spectra[6] of compound was recorded using KBr pellets on FTIR-Vector 22, Bruker, France at Indian Bureau of Mines, Nagpur. ^{1}H NMR spectra[7] was recorded on Bruker Avance-300 MHz spectrophotometer (chemical shift in δ ppm) using dimethyl sulfoxamide as solvent at NIPER, Chandigarh, India.

Step I: (a) Conversion of *p*-aminobenzoic acid into HCl salt of ammonium benzoyl chloride. (i)



p-aminobenzoic acid (i)

(b) Condensation of (i) with anthranilic acid.



(i) Anthranilic acid (ii) Synthesized dye [(4-ammonium chloride phenyl) amido, N-2 benzoic acid]

Synthetic and physico-chemical studies of dye: The HCl salt of *p*-aminobenzoic acid (5 g, 0.025 mol) was dissolved in dry pyridine (10 mL) and kept in ice to maintain temperature 0 to 5 ºC for 0.5 h. To it added thionyl chloride (2 mL, 0.0275 mol) dropwise maintaining temperature below 5 ºC. And the mixture of anthranilic acid (5 g, 0.0416 mol) in dry pyridine solution were prepared, poured portion wise to the above mixture and allowed to stand for 0.5 h at room temperature. The separated red dye filtered with suction and dried in room temperature. The red dye was recrystallized from mixture of *n*-butyl alcohol and N,N-dimethyl formamide (6:4) and stored in dessicator. Yield: 6.8 g (85.04 %), m.p. 280-282 ºC (*n*-butyl alcohol, N,N-dimethyl formamide, 6:4), R_f 0.67 (N,N-dimethyl formamide:benzene:water, 7:2:1), λ_{max} 322 nm (N,N-dimethyl formamide). IR spectra of red dye (KBr, cm^{-1}) 3123-2591 (NH_3^+ stretching), 3161-3024 (Ar-H stretching), 3433-3323 (Ar-NH stretching) 1643 (Ar-COOH stretching). NMR data of red dye (^{1}H NMR DMSO-d_6, δ ppm) 2.23 (s, 1H, NH_3^+), 10.30 (s, 1H, -COOH), 8.4 (s, 1H, NH), 7.78-10.3 (m, 8H, Ar-H).

RESULTS AND DISCUSSION

The synthesized dye shows drastic change in acid-base titration. The solubility of dye was found in dimethyl formamide/DMSO solvents. The titration was carried out using 0.1 M HCl as a titrate and 0.1 M NaOH as a titrant and *vice-versa* by using synthesized dye as an indicator and comparison was done using phenolphthalein and methyl red as an indicator.

Study showing comparison between dye, phenolphthalein and methyl red in acid-base titration. The results are listed Tables 1 and 2.

TABLE-1
SYNTHESIZED DYE AND PHENOLPHTHALEIN USED AS AN INDICATOR*

Indicator	Base	Acid	Average normality	Standard deviation
Dye	NaOH	HCl	0.956	0.3558
Phenolphthalein	NaOH	HCl	0.995	0.2854

*NaOH used as a titrant.

TABLE-2
SYNTHESIZED DYE AND METHYL RED USED AS AN INDICATOR*

Indicator	Base	Acid	Average normality	Standard deviation
Dye	NaOH	HCl	0.985	0.2891
Methyl red	NaOH	HCl	0.970	0.3850

*NaOH used as a titrate.

Results were comparable and reproducible. Synthesized dye have pH range in basic condition 8.5 to 10.8 and in acidic condition 4.6 to 5.2.

The present synthetic scheme for the formation of dyes from anthranilic acid is new. This method is economic, time saving, easy and have structure simplicity.

ACKNOWLEDGEMENT

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