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Synthesis of o-Nitro Phthal-as-Eins their Physico Chemical Investigations and Colour in Relation to their Constitutions

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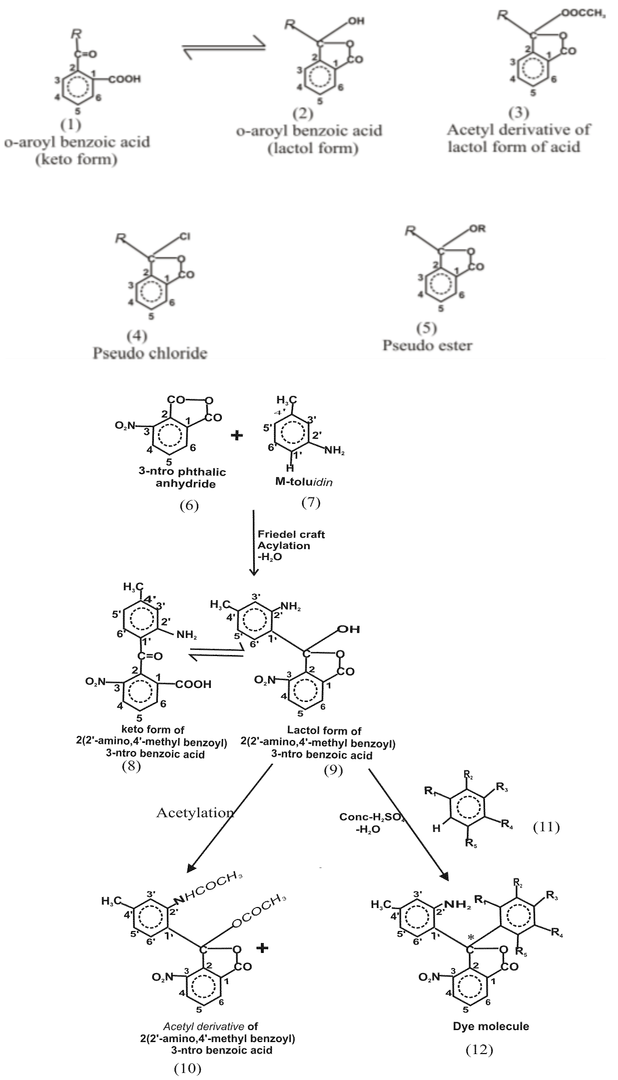
***Abstract*: Phthaleins having asymmetrical carbon atom (2 amino 4 methyl phenyl) 3 nitro phenolphthal-as-ein,(2 amino 4 methyl phenyl) resorcinol 3 nitro phthal-as-ein, (2 amino 4 methyl phenyl) catechol 3 nitro phthal-as-ein,(2 amino 4 methyl phenyl) hydroquinone 3 nitro phthal-as-ein, (2 amino 4 methyl phenyl) pyrogallol 3 nitro phthal-as-ein, (2 amino 4 methyl phenyl) phloroglucinol 3 nitro phthal-as-ein,have been found by condensing o (2'- amino, 4'-methyl phenyl benzoyl) 3 nitro benzoic acid with appropiate phenol.The structure of (2 amino 4 methyl phenyl) resorcinol phthal-as-ein, which was exist in two isomeric form, based on chemical reaction and spectral analysis has been discussed.**

***Keywords*: Phenyl, Phenol, Resorcinol, Pyrrogallol, phloroglucinol**

1. Introduction

Ortho benzoyl benzoic acid (1) has been found in two isomeric form the existence of cyclic isomer (lactol form) has been confirmed by various workers. The lactol form of gama keto acid more stable than their open chain isomer [1]. So on acetylation these lactol form of (2) to forms white crystalline acetyl derivative (3). The ring isomer of gama keto acid are also forms pseudo chloride (4)[2] and pseudo ester (5) [3-4]. Many other workers suggest that the gama keto acid have been explained on the basis of their cyclization to lactol. IR, Raman and NMR [5] spectra have been confirmed lactol form of the gama keto acid. The formation of 2-(2' amino 4' methyl benzoyl) 3nitro benzoic acid (8) from the substitution R of the cyclic or lactol form of gama keto acid by m-toluidin and its acetyl derivative (10) and Synthesis of its phenolic dyes from the condenses with various phenols and found a new series of asymmetrical 3 nitro phthal-as-ein. The condensing process undergo through the equilibrium process of lactol form of (2'amino, 4'methyl benzoyl) 3 nitro benzoic acid (9).

In this work the dyes prepared from the 2 (2'amino, 4'methyl benzoyl) 3 nitro benzoic acid may be represented by the following structures.



Graphical abstract

13- (2- amino, 4- methyl phenyl) phenol,3-nitro phthal-as-Ein. $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = OH$
14- (2- amino, 4- methyl phenyl) resorcinol,3-nitro phthal-as-einn. $R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OH$
15- (2- amino, 4- methyl phenyl) catechol,3-nitro phthal-as-Ein. $R_3 = R_4 = R_5 = H$, $R_1 = R_2 = OH$
16- (2- amino, 4- methyl phenyl) hydroquinone,3-nitro phthal-as-ein. $R_2 = R_3 = R_5 = H$, $R_1 = R_4 = OH$
17- (2- amino,4- methyl phenyl) pyrogallol ,3-nitro phthal-as-ein. $R_4 = R_5 = H$, $R_1 = R_2 = R_3 = OH$
18- (2-amino, 4- methyl phenyl) phloroglucinol ,3-nitr phthal-as-ein. $R_2 = R_4 = H$, $R_1 = R_3 = R_5 = O$
19- (2-acetyl amino, 4- methyl phenyl) diacetyl resorcinol,3-nitro phthal-as-ein. $R_2 = R_4 = R_5 = H$, $R_1 = R_3 = OCOCH_3$
20- (2- amino 3,5dibromo, 4- methyl phenyl)dibromo resorcinol ,3-nitro phthal-as-ein $R_5 = H$, $R_1 = R_3 = OH$; $R_2 = R_4 = Br$

Scheme-1

2. Result and discussion

2-(2'-amino 4'-methyl benzoyl) 3nitrobenzoic acid has also been found spectroscopically to exist as a mixture of keto (8) and lactol form(9).IR spectrum of the of the acid showed general absorption bands at 1625,1695,1745 cm^{-1} due to diaryl.ketonic >C=O, carbxyl >C=O, lactonic >C=O respectively. Absorption peaks due to Carboxyl-OH and lactol-OH appear at 2650cm^{-1} (week), 3300 (broad) cm^{-1} , and a peak appear at 3350 cm^{-1}due to amino group $–NH_2$. In the NMR spectrum of the acid showed the general peaks at δ 1.9-3.15 m, 6.55 s ,7.8 s ,4.35 br due to 6, 2, and 3 protons of unsymmetrical aromatic, $-N\underline{H}_2$,$-C\underline{H}_3$ and lactol protons respectively.

IR spectrum of the acetyl derivative of the acid shows notable absorption band at 1785 cm^{-1} which may be assigned lactonic >C=O. peaks at 1750,1250,1220,1030 are due to presence of acetate groups. In the NMR spectrum of the acetyl derivative at δ 2.05-3.35 m, 3.2 s ,7.7 s, due to 6,1and 3 protons of unsymmetrical aromatic, NH and $-C\underline{H}_3$, there is no signal at δ 6.55 s, 4.35 (present in the NMR spectrum of the acid) but there are two new signals at 7.85 s, 7.65 s, due to ($3-NH-CO-C\underline{H}_3$ protons), ($-CO-C\underline{H}_3$ protons) acetate groups.

On the basis of above spectral studies it has been confirm that the possesses in acyclic form and its formation takes place the lactol form (9) of the acid (8). The dye was prepared by condensing 2-(2'amino 4' methyl benzoyl) 3nitro benzoic acid (9) of acid (8) with phenols (11) in presence of a few drops of concentrated sulphuric acid as the condensing agent as described above. The purity of the dye was tested by paper chromatography. Their structure have been confirmed on the basis of elemental analysis, acetylation bromination and caustic potash treatment. Although in this paper described the structure of 3-(2-amino, 4-methyl phenyl)-3-(2,4, di hydroxy phenyl) 3ntro phthal-as-ein(14) having molecular formula $C_{21}H_{16}N_2O_6$ molecular weight 392,On acetylation yielded tri acetyl derivative (19) indicating the presence of only two phenolic groups. When brominated with calculated amount of bromine, the dye gave a tetra bromo derivative (20) confirming the presence of a molecule of resorcinol in the dye. On caustic potash treatment the dye yielded a molecule of 2-(2'amino, 4'methyl benzoyl) 3nitro benzoic acid (8) and a molecule of resorcinol (21) with an excess of bromine, the dye yielded a molecule of the same acid and a molecule of tri bromo resorcinol (22). On the basis of above chemical evidences, Structure (14) has been assigned to the dye.

The absorption maxima ($\boldsymbol{\lambda}_{max}$) of phthal-as-ein are given in table (2). Table three shows the ($\boldsymbol{\lambda}_{max}$) true phthal-as-ein prepared in same. Absorption maxima of phthal-as-ein 11, 12 and 18 have been compared with those of phenolphthalein, fluorescein and eosin respectively and a self-possession has been studied.

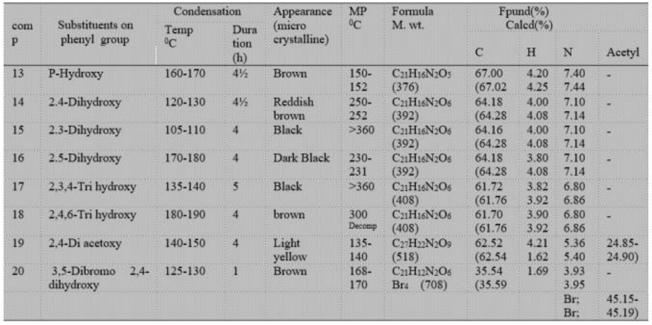
3. Materials and Methods

Required material for synthesis are nitro phthalic anhydride, sodium carbonate, m- toluidine, sulfuric acid as dehydrating agent, bromine, caustic potash, sodium acetate, anhydrous $AlCl_3$ used as catalyst, acetic anhydride for acetylation, acetone, chloroform, ethyl alcohol, benzene as solvent, gama keto acid prepared by Friedel-Crafts acylation reaction and various phenols like phenol, catechol, resorcinol, hydroquinol, pyrogallol, phloroglucinol are also used. The purity of dyes was tested by paper chromatography by descending technique. The UV and visible spectroscopy has been recorded using model DU Beckman Spectrophotometer in ethanol.

4. Experimental

The required intermediates and final compounds were synthesized using the standard synthetic protocols. The procedures for the synthesis of Intermediates and target dyes along with their structural characterization data are given below.

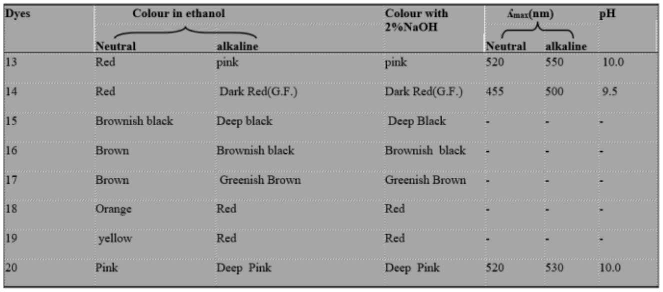
Table 1
Characterization data of compounds



com p	Substituents on phenyl group	Condensation Temp °C	Dura tion (h)	Appearance (micro crystalline)	MP °C	Formula M. wt.	Fpund(%) Calcd(%) C	H	N	Acetyl
13	P-Hydroxy	160-170	4½	Brown	150- 152	$C_{21}H_{16}N_2O_5$ (376)	67.00 (67.02	4.20 4.25	7.40 7.44	-
14	2.4-Dihydroxy	120-130	4½	Reddish brown	250- 252	$C_{21}H_{16}N_2O_6$ (392)	64.18 (64.28	4.00 4.08	7.10 7.14	-
15	2.3-Dihydroxy	105-110	4	Black	>360	$C_{21}H_{16}N_2O_6$ (392)	64.16 (64.28	4.00 4.08	7.10 7.14	-
16	2.5-Dihydroxy	170-180	4	Dark Black	230- 231	$C_{21}H_{16}N_2O_6$ (392)	64.18 (64.28	3.80 4.08	7.10 7.14	-
17	2,3,4-Tri hydroxy	135-140	5	Black	>360	$C_{21}H_{16}N_2O_6$ (408)	61.72 (61.76	3.82 3.92	6.80 6.86	-
18	2,4,6-Tri hydroxy	180-190	4	brown	300 Decomp	$C_{21}H_{16}N_2O_6$ (408)	61.70 (61.76	3.90 3.92	6.80 6.86	-
19	2,4-Di acetoxy	140-150	4	Light yellow	135- 140	$C_{27}H_{22}N_2O_9$ (518)	62.52 (62.54	4.21 1.62	5.36 5.40	24.85- 24.90)
20	3,5-Dibromo 2,4-dihydroxy	125-130	1	Brown	168- 170	$C_{21}H_{12}N_2O_6$ Br_4 (708)	35.54 (35.59	1.69	3.93 3.95	-
									Br: Br:	45.15- 45.19)

All the dyes crystallized from rectified ethanol. (a) Excess of phenol after condensation was removed by steam distillation.

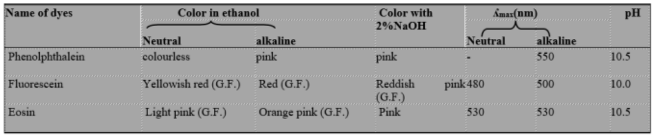
Table 2
Absorbtion maxima of 3-(2-amino, 4-methyl phenyl)-3-(substituted phenyl phthalide:-. (G.F. = Green fluorescence)



Dyes	Colour in ethanol		Colour with 2%NaOH	ʎ$_{max}$(nm)		pH
	Neutral	alkaline		Neutral	alkaline	
13	Red	pink	pink	520	550	10.0
14	Red	Dark Red(G.F.)	Dark Red(G.F.)	455	500	9.5
15	Brownish black	Deep black	Deep Black	-	-	-
16	Brown	Brownish black	Brownish black	-	-	-
17	Brown	Greenish Brown	Greenish Brown	-	-	-
18	Orange	Red	Red	-	-	-
19	yellow	Red	Red	-	-	-
20	Pink	Deep Pink	Deep Pink	520	530	10.0

(-) correct ʎmax could not be measured due to decomposition of these dyes in solution.

Table 3
Absorption maxima of known Phthaleins



Name of dyes	Color in ethanol		Color with 2%NaOH	ʎ$_{max}$(nm)		pH
	Neutral	alkaline		Neutral	alkaline	
Phenolphthalein	colourless	pink	pink	-	550	10.5
Fluorescein	Yellowish red (G.F.)	Red (G.F.)	Reddish pink (G.F.)	480	500	10.0
Eosin	Light pink (G.F.)	Orange pink (G.F.)	Pink	530	530	10.5

Synthesis of 2-(2'-amino 4'-methyl benzoyl)3nitro benzoic acid

The acid was prepared by carrying out Friedel-Craft reaction between m toluidin (dry AR 100ml.) and 3-nitro phthalic anhydride (15.0g, 0.1mole) with anhydrous aluminium chloride (24g about, 0.2mole) used as catalyst. The reaction was carried out in one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 25 degree centigrade by adding anhydrous aluminium chloride in instalments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evaporation of hydrogen chloride ceased.

The heavy dark coloured complex was decomposed by adding 30 ml of concentrated hydrochloric acid (in 250 ml ice cold water). The excess of m-toluidin was removed by steam distillation. The residue was extracted three four times with boiling 10% solution of Na_2CO_3 and filtered. The acid was precipitated from the filtrate by the gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and crystallized from acetone. The white crystalline acid has m.p. 140-141^0 C, yield 20g. It is soluble in benzene, chloroform, acetone and ethanol.

Anal. For : $C_{15}H_{12}N_2O_5$ (molecular weight 300)
Calc. : C, 60.2; H, 4.0; N,9.33;
Found : C, 60.0; H, 3.8; N,9.30;

2-(2'-amino 4'-methyl benzoyl) 3 nitro benzoic acid was prepared according to reported procedure. Its acetyl derivative prepared by refluxing it with acetic anhydride in presence of fused sodium acetate. The phenols (phenol, resorcinol, catechol, hydroquinone, pyrogallol and phloroglucinol) have been taken in slight excess of molecular proportion than the acid (7) and concentrated sulfuric acid (4-5 drops) has been used as condensing agent throughout. Comparable to phthalides, the condensation is supposed to have taken place as given in scheme 1.

Synthesis of 3-(2-amino, 4-methyl phenyl)-3-(2,4, di hydroxy phenyl)3nitro phthalide (14)

It was prepared by condensing an intimate mixture of the acid (3.0 g) and resorcinol (3.0g) in an oil bath in presence of 7-8 drops of concentrated sulphuric acid at 120-130^{0}C for about four and half hour till the molten mass became hard and brittle on cooling. The condensed mass was crushed and washed with an excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was precipitated from filtrate by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 100^{0}C and then in a vacuum desiccator, yield 3.0g. The redish brown microcrystalline dye having m.p. 250-252^{0}C is, soluble in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is red which alters to dark red with green fluorescence on adding a drop of an alkali. In strong basic medium, reddish brown colour is obtained.

Anal. For : C_{21} $H_{16}N_2O_6$ (molecular weight 392)
Calc. : C, 64.28; H, 4.08;N,7.14;
Found : C, 64.18; H, 4.00;N,7.10;

Paper chromatography of dyes (13)

On the test paper Whatman No 1,1 butanol-ammonia was allowed to run for 12 h (descending) to give two corresponding red pink spot of the dye (13) and reference dye phenolphthalein, R_f : (13), 0.89 phenolphthalein,0.91 (R_f 0.92).

Acetylation of dye (14)

The dye (2 amino,4 methyl phenyl) resorcinol 3nitro phthal-as-ein (1.0g) and fused sodium acetate (3.0g) with 15.0 ml of freshly distilled acetic anhydride were taken in a 50 ml round bottom flask fitted with an air condenser. The contents were refluxed at 135-1400C for about four hours. The hot contests poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon the light yellow solid settled down. It was filtered, washed well and dried.

The crude product was treated with animal charcoal and crystallized from aqueous ethanol and a little acetic acid. It was dried in an oven at 45^{0}C and then over phosphorus pentoxide under reduced pressure, yield 0.80g. The crystalline derivative is light yellow coloured m.p. 117-119^{0}C. Its ethanolic solution is red which turns into red with green fluorescence on addition of alkali.is soluble in benzene, ethanol, chloroform, acetone and acetic acid

Anal. For: C_{27} $H_{22}N_2O_9$ or $C_{21}H_{13}N_2O_6$ $(OCCH_3)_3$m. wt 518)
Calc. : Acetyl, 24.90;
Found : Acetyl, 24.85

5Brominationof dye (14)

The dye (2-amino,4-methyl phenyl)-resorcinol 3 nitro-phthal-as-ein (1.0g) was dissolved in minimum quantity of glacial acetic acid and 15ml of a 10% solution of bromine in glacial acetic acid was slowly added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 125-130^{0}C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange powder settled down. It was filtered and washed well with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye by gradual addition of dilute hydrochloric acid. The crude brominated dye was finally purified by crystallization from aqueous ethanol and dried at 80^{0}C in and oven and then in a vacuum desiccator, yield, 0.85g. The brown crystalline compound having m.p. 168-170^{0}C. Its ethanolic solution is pink which turns into deep pink with green fluorescence on addition of alkali.is soluble in benzene, ethanol, chloroform, acetone and acetic acid.

Anal. For: $C_{21}H_{12}N_2O_6Br_4$ (m.wt. 708)
Calc. ; Br, 45.19;
Found ; Br, 45.15;

Caustic potash fusion of (2-amino,4-methyl, phenyl) resorcinol ,3-nitro phthal -as-ein

Potassium hydroxide pallets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The dye (1.0) was then added to it. The contents were heated for about four hours till the darkened colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. The dark residue (I) settled down on just neutralizing the alkali. It was filtered and washed well with water. The filtrate, when acidified further by adding excess of dilute hydrochloric acid gave white precipitate (II), which was filtered and washed with water. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Residue-I

It was identified and confirmed to be the unreacted dye from its colour reaction and determination of the mixed melting point with the original dye.

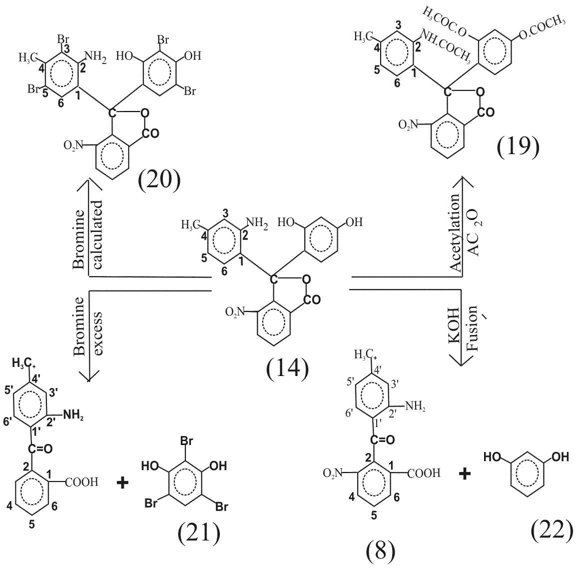
Residue-II

It was acidic in nature and gave positive tests for the presence of carboxylic groups. It was identified as 2-(2'amino 4'methyl benzoyl) 3-nitro benzoic acid and confirmed by mixed melting point determination (m.p.140-141^{0}C) and by superimposition of the IR spectra of the authentic sample.

Residue-III

The purified sample melted at 110^{0}C. It gave positive tests with ferric chloride, Fehling's solution and ammonia silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are given below.



5. Conclusion

We can therefore safely conclude that the color of resorcinol phthalide can be rationalized both in the solid state (reddish brown) and in neutral medium (λ-max 455-520nm). But in the alkaline medium the polar forms of the molecule become available in solution so that the number of resonating structures of the molecule increases. As a result, more crowded and depressed energy levels are produced i.e. a bathochromic shift occurs. As a matter of fact, all these dyes yield absorption band at (455-520nm) in neutral medium. However, in slightly alkaline medium the λ_{max} are shifted to the range of (530-550nm).

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