

# Synthesis and Studies of New Comparable of 3-(2-amino, 4-methyl phenyl) -3- (Substituted Phenyl) Phthalide

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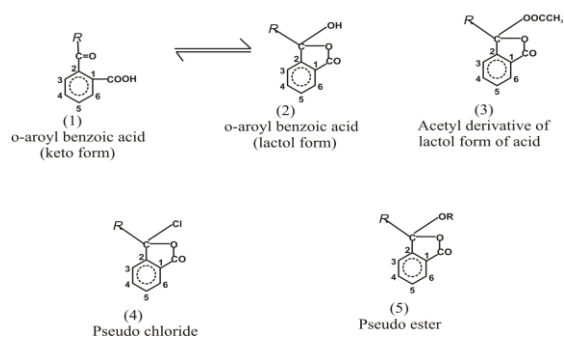
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**Abstract:** A new series of dyes have been synthesized by condensation 2-(2'-amino 4'-methyl benzoyl) benzoic acid with various phenol such as mono, di and tri hydric phenol using concentrated sulphuric acid as the condensing agent. The resulting compounds are substituted phthalides having central tri phenyl methane asymmetrical carbon atom attached to different phenyl rings such as 3-(2-amino,4-methyl phenyl)-3-(phydroxy phenyl) phthalide, 3-(2-amino, 4-methyl phenyl)-3-(2,4-dihydroxy phenyl) phthalide, 3-(2-amino, 4-methyl phenyl)-3-(2,3-dihydroxy phenyl) phthalide, 3-(2-amino, 4-methyl phenyl)-3-(2,5-dihydroxy phenyl) phthalide, 3-(2-amino, 4-methyl phenyl)-3-(2,3,4-trihydroxy phenyl) phthalide and 3-(2-amino, 4-methylphenyl) -3-(2,4,6-trihydroxyphenyl) phthalide. The resulting phthalide were characterized through Electronic spectra data in ethanol (neutral and alkaline) are compared to those of some known phthalins. UV-Visible elemental and spectral analysis. The absorption spectra properties of as prepared phthalides were investigated in 95% Ethanol, attempt to evaluate spectral behaviors.

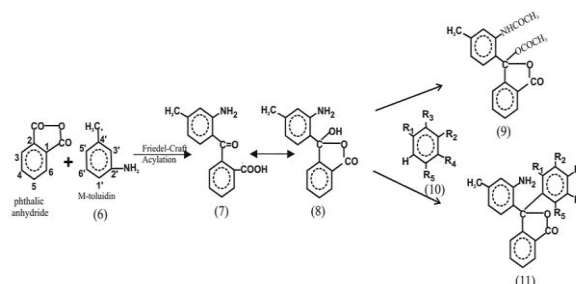
**Keywords:** Toluidin Phthalide, Phenyl, Phenol, Resorcinol, Pyrogallol, Phloroglucinol,

## 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 gamma 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 gamma keto acid are also forms pseudo chloride (4)[2] and pseudo ester (5) [3-4]. Many other workers suggest that the gamma 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 gamma keto acid. The formation of 2-(2' amino 4' methyl benzoyl) benzoic acid (7) from the substitution R of the cyclic or lactol form of gamma keto acid by m-toluidin and its acetyl derivative (8) and Synthesis of its phenolic dyes from the condenses with various phenols and found a new series of asymmetrical Innovative Comparable of phthalide. The condensing process undergo through the equilibrium process of lactol form of (ortho aroyl) benzoic acid (7).



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



Graphical abstract:

- (12)  $R_1 = R_2 = R_4 = R_5 = H, R_3 = OH,$
- (13)  $R_2 = R_4 = R_5 = H, R_1 = R_3 = OH,$
- (14)  $R_3 = R_4 = R_5 = H, R_1 = R_2 = OH,$
- (15)  $R_2 = R_3 = R_5 = H, R_1 = R_4 = OH,$
- (16)  $R_4 = R_5 = H, R_1 = R_2 = R_3 = OH,$
- (17)  $R_2 = R_4 = H, R_1 = R_3 = R_5 = OH,$
- (18)  $R_2 = R_4 = R_5 = H, R_1 = R_3 = OCOCH_3,$
- (19)  $R_5 = H, R_1 = R_3 = OH; R_2 = R_4 = Br$

Scheme -1

## 2. Result and discussion

2-(2'-amino 4'-methyl benzoyl) benzoic acid has also been found spectroscopically to exist as a mixture of keto (7) and lactol form(8). IR spectrum of the of the acid showed general absorption bands at 1695, 1700, 1715  $\text{cm}^{-1}$  due to diaryl ketonic  $>\text{C}=\text{O}$ , carbonyl  $>\text{C}=\text{O}$ , lactonic  $>\text{C}=\text{O}$  respectively. Absorption peaks due to Carboxyl-OH and lactol-OH appear at 2665  $\text{cm}^{-1}$  (weak), 3440 (broad)  $\text{cm}^{-1}$ , and a peak appear at 3350  $\text{cm}^{-1}$  due to amino group  $-\text{NH}_2$ . In the NMR spectrum of the acid showed the general peaks at  $\delta$  3.0-3.15 m, 6.45 s, 7.70 s, 4.35 br due to 3, 2, and 3 protons of unsymmetrical aromatic,  $-\text{NH}_2$ ,  $-\text{CH}_3$  and lactol protons, respectively.

IR spectrum of the acetyl derivative of the acid shows notable absorption band at 1695  $\text{cm}^{-1}$  which may be assigned lactonic  $>\text{C}=\text{O}$ . peaks at 1760, 1240, 1210, 1030 are due to presence of acetate groups. Peaks presence in the IR spectrum of the acid at 3440, 2665, 1695, 1735  $\text{cm}^{-1}$  found to be absent in the IR spectrum of the acetyl derivative of the acid. In the NMR spectrum of the acetyl derivative at  $\delta$  2.8-3.20 m, 3.2 s, 7.55 s due to 3, 1 and 3 protons of unsymmetrical aromatic, NH and  $-\text{CH}_3$ , there is no signal at  $\delta$  6.6 s, 4.35 (present in the NMR spectrum of the acid) but there are two new signals at 7.90 s, 7.75 s, due to (3-NH-CO- $\text{CH}_3$  protons), ( $-\text{CO}-\text{CH}_3$  protons) acetate groups.

On the basis of above spectral studies it has been confirmed that the possesses in acyclic form and its formation takes place the lactol form (8) of the acid (7). The dye was prepared by condensing 2-(2'-amino 4' methyl benzoyl) benzoic acid (8) of acid (7) with phenols (9) 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 has 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) phthalide (13) having molecular formula  $\text{C}_{21}\text{H}_{17}\text{NO}_4$  molecular weight 347, On acetylation yielded tri acetyl derivative (18) indicating the presence of only two phenolic groups. When brominated with calculated amount of bromine, the dye gave a tetra bromo derivative (19) 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) benzoic acid (7) and a molecule of resorcinol (20) with an excess of bromine, the dye yielded a molecule of the same acid and a molecule of tri bromo resorcinol (21). On the basis of above chemical evidences, Structure (13) has been assigned to the dye.

The absorption maxima ( $\lambda_{\text{max}}$ ) of phthalide are given in table 2. Table 3 shows the ( $\lambda_{\text{max}}$ ) true phthalide prepared in same. Absorption maxima of phthalide 12, 13 and 19 have been compared with those of phenolphthalein, fluorescein and eosin respectively and a self-possession has been studied.

## 3. Material and methods

Required material for synthesis are phthalic anhydride, sodium carbonate, m- toluidine, sulfuric acid as dehydrating agent, bromine, caustic potash, sodium acetate, anhydrous  $\text{AlCl}_3$  used as catalyst, acetic anhydride for acetylation, acetone, chloroform, ethyl alcohol, benzene as solvent, gamma 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.

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

Table 1  
Characterization data of compounds

comp	Substituents on phenyl group	Condensation		Appearance (micro crystalline)	MP $^{\circ}\text{C}$	Yield %	Formula M. wt.	Elemental (%)			
		Temp $^{\circ}\text{C}$	Duration (h)					C	H	N	Acetyl
12	P-Hydroxy	160-170	4½	Brown	231-232	45	$\text{C}_{21}\text{H}_{17}\text{NO}_3$ (331)	76.00 (76.13)	5.10 (5.13)	4.25 (4.20)	-
13	2,4-Dihydroxy	155-165	4½	Reddish brown	>360	86	$\text{C}_{21}\text{H}_{17}\text{NO}_4$ (347)	72.2 (72.62)	4.86 (4.90)	4.00 (4.03)	-
14	2,3-Dihydroxy	105-110	4	Black	>360	43	$\text{C}_{21}\text{H}_{17}\text{NO}_4$ (347)	72.54 (72.62)	4.84 (4.90)	4.00 (4.03)	-
15	2,5-Dihydroxy	165-180	4	Black	230-231	72	$\text{C}_{21}\text{H}_{17}\text{NO}_4$ (347)	72.52 (72.62)	4.89 (4.90)	4.01 (4.03)	-
16	2,3,4-Tri hydroxy	135-140	5	Black	>327	35	$\text{C}_{21}\text{H}_{17}\text{NO}_5$ (363)	69.35 (69.42)	4.65 (4.68)	3.76 (3.85)	-
17	2,4,6-Tri hydroxy	210-215	4	Dark brown	>300	59	$\text{C}_{21}\text{H}_{17}\text{NO}_5$ (363)	69.40 (69.42)	4.65 (4.68)	3.82 (3.85)	-
18	2,4-Di acetoxy	135-140	4	Light yellow	48-50	14	$\text{C}_{21}\text{H}_{25}\text{NO}_7$ (473)	68.40 (68.49)	4.80 (4.86)	2.80 (2.95)	27.22 (27.27)
19	3,5-Dibromo 2,4-dihydroxy	125-130	1	Dirty orange	120-125	12	$\text{C}_{21}\text{H}_{13}\text{NO}_4$ $\text{Br}_4$ (663)	43.00 (43.07)	4.10 (4.12)	2.00 (2.11)	-
											Br, 48.20 Br, 48.20

Table 2

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

Dyes	Colour in ethanol		Colour with 2%NaOH	$\lambda_{\text{max}}$ (nm)		pH
	Neutral	alkaline		Neutral	alkaline	
	12	Light yellow	pinkish	pinkish	510	530
13	Yellowish orange	Yellowish Orange(G.F.)	Yellowish Orange(G.F.)	460	495	9.8
14	Brownish black	Brownish black	Black	410	650	10.5
15	Brown	Brownish violet	Brownish violet	-	-	-
16	Wine	violet	Blue black	-	-	-
17	Brown	Dark Brown	Dark Brown	-	-	-
18	Light yellow	Reddish Green(G.F.)	Reddish Green	-	-	-
19	Yellowish Orange	Reddish Orange(G.F.)	Reddish Orange(G.F.)	540	530	9.0

(-) correct  $\lambda_{\text{max}}$  could not be measured due to decomposition of these dyes in solution.

### A. Synthesis of 2-(2'-amino 4'-methyl benzoyl) benzoic acid

2-(2'-amino 4'-methyl benzoyl) benzoic acid was prepared according to reported procedure [18] 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.

Table 3  
Absorption maxima of known phthalins

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

### B. Synthesis of 3-(2-amino, 4-methyl phenyl)-3-(2,4, di hydroxy phenyl) phthalide (13)

It was prepared by condensing an intimate mixture of the acid (5.0 g) and resorcinol (3.0g) in the oil bath in presence 7-8 drops of concentrated sulfuric acid at 120-130°C for about four and half hours 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 by adding slowly dilute hydrochloric acid with constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 100°C and then in vacuum desiccators, (5.4g,56% of the theoretical yield). The reddish brown microcrystalline dye having m. p. 361°C is, soluble in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is yellow which alters to brownish red with green fluorescence on adding a drop of an alkali. In strong basic medium, reddish brown color is obtained. Found: C, 72.52; H, 4.88; N, 4.00; % molecular weight 347 (Rast). Calculated for  $C_{21}H_{17}NO_4$ : C, 72.62; H, 4.89; N,4.03. The preparation of rest of the dyes, given in table 1 has been done in the identical manner as already described.

### C. Paper chromatography of dyes (12)

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).

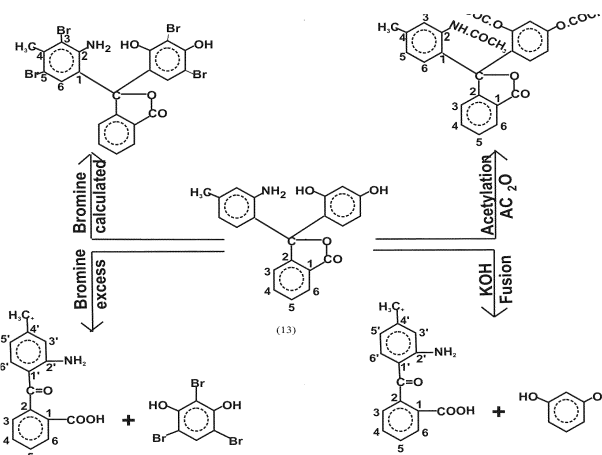
### D. Acetylation of dye (13)

The dye 3-(2-amino, 4-methyl phenyl)-3-(2,4, di hydroxy phenyl) phthalide (1.0g) was refluxed with acetic anhydride (15 ml) at 135-140°C for 4 h to give light yellow micro crystalline tri acetyl derivative (0.62g), mp,48-50°C (from rectified ethanol).It is soluble in ethanol, acetone, and acetic acid . Found: C, 68.40; H, 4.80; N, 2.80; Acetyl, 27.22 calculated for  $C_{21}H_{16}NO_4(OCCH_3)_3$ : C, 68.49; H, 4.86; N, 2.95; Acetyl, 27.27%.

### E. Bromination of dye (13)

The dye (13) (1.0g) and 10% solution of bromine in glacial acetic acid (10) were refluxed at 125-130°C for 1 h. The contents were cooled and diluted with minimum quantity of

distilled water. A dirty orange powder tetra bromo compound (0.80g), mp, 120-125°C Its ethanol solution is yellowish orange which turns into reddish orange with green fluorescence on addition of alkali. Found Br, 48.23; calculated for:  $C_{21}H_{13}NO_4Br_4$ ; Br, 48.26.



Scheme-2

### F. Caustic potash fusion of Dye (13)

Potassium hydroxide pellets (10.0g) were taken in a crucible and heated with a few drops of water to make a paste. The resorcinol dye (1.0g) was then added to it. The contents were heated for about four hours till the darkened color 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) benzoic acid and confirmed by mixed melting point determination (m.p.138-140°C) and by superimposition of the IR spectra of the authentic sample.

**Residue-III:** The purified sample melted at 108-110°C. It gave positive tests with ferric chloride, Fehling's solution and ammoniacal silver nitrate. It gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

## 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 ( $\lambda$ -max 460-495nm). 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 (460-495nm) in neutral medium. However, in slightly alkaline medium the  $\lambda_{\max}$  are shifted to the range of (490-520nm).

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