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Synthesis and Studies of Innovative Analogous of 3-(2-amino, 4-methyl phenyl)-3-(Substituted Phenyl) Tetrachlorophthalide

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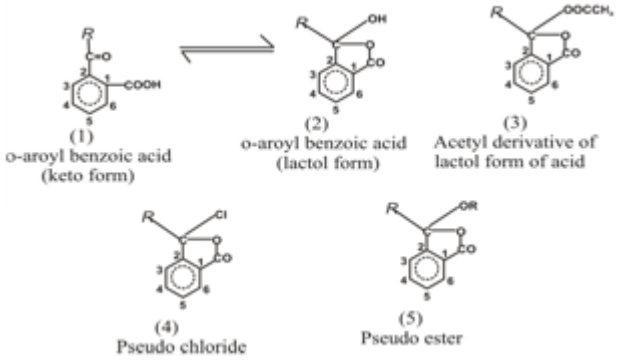
Abstract: ***A new series of dyes have been synthesized by condensation 2-(2'-amino 4'-methyl benzoyl) tetra chloro benzoic acid with various phenol such as mono, di and tri hydric phenol using concentrated sulphuric acid as the condensing agent. The resulting compounds are substituted tetra chlorophthalides having asymmetrical carbon atom attached to different phenyl rings such as 3-(2-amino, 4-methyl phenyl)-3-(phydroxy phenyl) tetra chlorophthalide, 3-(2-amino, 4-methyl phenyl)-3-(2, 4-dihydroxy phenyl) tetra chlorophthalide, 3-(2-amino, 4-methyl phenyl)-3-(2, 3-dihydroxy phenyl) tetra chlorophthalide, 3-(2-amino, 4-methyl phenyl)-3-(2, 5-dihydroxy phenyl) tetra chlorophthalide, 3-(2-amino, 4-methyl phenyl)-3-(2, 3, 4-trihydroxy phenyl) tetra chlorophthalideand3-(2-amino, 4-methylphenyl)-3-(2, 4, 6-trihydroxyphenyl) tetra chlorophthalide. The absorption spectra properties of as prepared tetra chlorophthalides were investigated in 95% Ethanol.***

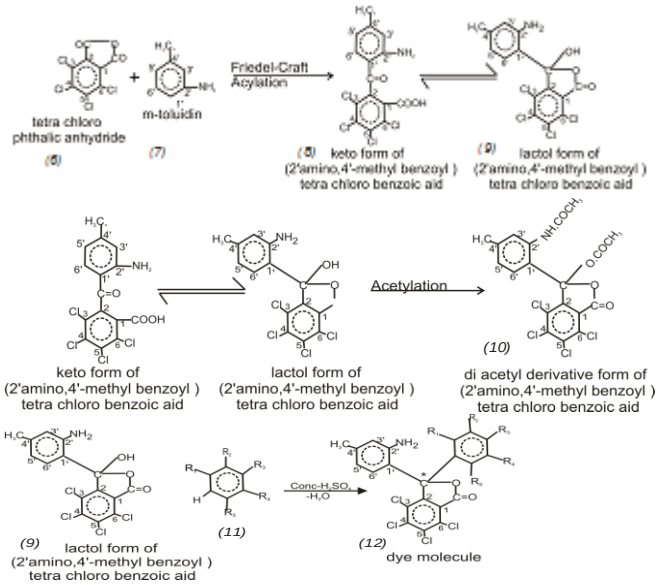
Keywords: ToluidinTetrachlorophthalic AnhydridePhenyl, Phenol, Resorcinol, Pyrrogallol, phloroglucinol.

1. Introduction

In ancient times, the materials used to produce colours were obtained from vegetable or animal sources. Three of the most prized colours: one of the blue of Indigo which Egyptians were using as early as 3000 B.C., others Turkey red or Alizarin and yellow of saffron obtained from the root of Madder (Rubiatinctorum) and Carthamustinctorious respectively. Human races have the ability to perceive colours since the dawn of civilization and man has attempted to reproduce the colours of nature for both aesthetic and purely functional purposes. Commercial importance of colouring matters has considerable interest shown in the theoretical and empirical evaluation of relationship between colour and molecular structure. The modern lifestyle enjoy dyes, pigments and their applications in the field of science, art, philosophy, psychologybiology[1], medicine[2], engineering, architecture and technology[3]. In nineteen century Hofmann had observed that aniline dyes gave red colour under certain conditions. Furthermore Perkin[4] oxidized aniline sulphate with potassium dichromate and obtained a purple dye called mauve. Since then the progress in the field of dyes has been very rapid[5-6] .To list a few milestones in the progress, direct dyes from azo compounds for cotton were introduced in 1880, Sulfur colours from coal tar derivative in 1893, Anthraquinone dye and Vat dyes in 1901, Azoic dyes or Ice colours in 1911, Acetoacetanilides in 1923, Phthalocyanines in 1934, Fluorescent Brightning agents in 1940 and Fibre Reactive Procion dyes in 1956. Thus natural dyestuffs were almost completely displaced by synthetic colorants. Fundamental research on new dyes is constantly in progress [7-10] and thus synthetic dyes are dominating now. Recently novel analogous of tetrachlorophthaleins were also prepared by Gupta et.al.[11-12] and Beg & coworkers. The above alteration in the phenolic part of a tetrachlorophthalide enables us to obtain Innovative Analogous of tetrachlorophthalide, in which the central C atom is attached to two different rings (nuclei). These would be expected to give rise to no colour or less intense colour than the corresponding tetrachlorophthalide. In order to achieve this objective, phthalic anhydride is to be replaced by a properly 2 (2'amino, 4'methyl benzoyl tetrachloro benzoic acid.New series of tertachlorophthalide. Ortho benzoyl benzoic acid (1) has been found in two isomeric forms the existence of cyclic isomer (lactol form) has been confirmed by various workers. The lactol forms of gamaketo acid more stable than their open chain isomer .So on acetylation these lactol form of (2) to forms white crystalline acetyl derivative (3). The ring isomer of gamaketo acid are also forms pseudo chloride (4) and pseudo ester (5)[13]. Many other workers [14] suggest that the gamaketo acid have been explained on the basis of their cyclization to lactol. IR[15], Raman and NMRspectra have been confirmed lactol form of the gamaketo acid. The formation of 2-(2'amino, 4'methylbenzoyl)tetra chloro benzoic acid (7) from the substitution R of the cyclic or lactol form of gamaketo acid by toluidin and its acetyl derivative (10) and Synthesis of its phenolic tetrachlorophthalide from the condenses with various phenols and found a new series of asymmetrical Innovative Analogous oftetrachlorophthalide. The condensing process undergo through the equilibrium process of lactol form of 2-(2'amino, 4'methylbenzoyl)tetra chloro benzoic acid (7).



In this work the dyes prepared from the 2-(2'amino, 4'methylbenzoyl) tetra chloro may be represented by the following structures.



Graphical abstract

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

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 acid showed general absorption bands at1695, 1700, 1735 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 2665cm^{-1} (week) , 3440 (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 3.30-3.15m, 6.45 s , 7.70 s , 4.35 br due to 3, 2, and3 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 1760, 1240, 1210, 1030 are due to presence of acetate groups. Peaks presence in the IR spectrum of the acid at 3100, 2655, 1680, 1745 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 δ 2.4-3.20 m, 3.2s , 7.75 s , 4.35 br due to 3and 3 protons of unsymmetrical aromatic, -NH-and -$C\underline{H}_3$, there are two new signals at 7.90 s , 7.75 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 (7).The dye was prepared by condensing 2-(2'amino 4' methyl benzoyl) benzoic (9) of acid (8) with phenols (10) 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. But here described the structure of 3-(2-amino, 4-methyl phenyl)-3-(2, 4, di hydroxy phenyl) tetra clorophthalide(14) having molecular formula $C_{21}H_{13}NO_4Cl_4$ molecular weight 485, On acetylation yielded tri acetyl derivative (21) 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) tetra chloro benzoic acid (8) and a molecule of resorcinol (23) 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 (λ_{max}) of tetra chlorophthalide are given in table (2).Table three shows the (λ_{max}) true phthalide prepared in same.

3. Material and Methods

Required material for synthesis are tetra chlorophthalic anhydride, sodium carbonate, toluidin, 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, gamaketo 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.

4.1 *Synthesis of 2-(2'amino, 4'methyl benzoyl)tetra chloro benzoic acid*

2(2'amino, 4'methyl benzoyl) tetrachloro benzoic acid was prepared according to reported procedure [35] 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 (9) 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

4.2-*Synthesis of 3-(2'amino, 4'methyl benzoyl)-3-(2, 4, dihydroxy phenyl) tetra chlorophthalide*(15):-

It was prepared by condensing an intimate mixture of the 2(2'amino, 4'methyl benzoyl)tetra chloro benzoic acid (5.0

g) and resorcinol (3.0g) in the oil bath in presence 5-6 drops of concentrated sulfuric acid at 120-130^{0}C for about four and

Table I: Characterization data of compounds

comp	Substituents on phenyl group	Condensation		Appearance (micro crystalline)	MP ^{0}C	Formula M. wt.					Fpund(%) Calcd(%)
		Temp ^{0}C	Duration (h)				C	H	N	Cl	Acetyl
13	P-Hydroxy	160-170	4½	Brown	300	$C_{21}H_{13}NCl_4O_3$ (469)	53.73 (53.60	2.74 2.77	2.96 2.98	30.25 30.27)	-
14	2.4-Dihydroxy	120-130	4	Reddish brown	283-285	$C_{21}H_{13}NCl_4O_4$ (485)	51.85 (51.95	2.65 2.68	3.86 3.88	29.26 29.27)	-
15	2.3-Dihydroxy	125-130	4	Brownish black	360	$C_{21}H_{13}NCl_4O_4$ (485)	51.84 (51.95	2.66 2.68	3.86 3.88	29.24 29.27)	-
16	2.5-Dihydroxy	175-180	4	Black	<280	$C_{21}H_{13}NCl_4O_4$ (485)	51.84 (51.95	2.64 2.68	3.85 3.88	29.24 29.27)	-
17	2, 3, 4-Tri hydroxy	150-160	5	Black	>330	$C_{21}H_{13}NCl_4O_5$ (501)	50.24 (50.29	2.54 2.29	2.76 2.79	28.28 28.24)	-
18	2, 4, 6-Tri hydroxy	200-210	4	Blackish brown	282-284	$C_{21}H_{13}NCl_4O_5$ (501)	50.22 (50.29	2.55 2.29	2.76 2.79	28.29 28.24)	-
19	2, 4-Di acetoxy	130-140	4	Pale yellow	132-134	$C_{27}H_{19}NCl_4O_7$ (661)	53.00 53.02	3.08 3.10	2.25 2.29	23.22 22.24)	21.19 21.11)
20	3, 5-Dibromo 2, 4-dihydroxy	125-135	1	Red	130-135	$C_{21}H_9NCl_4Br_4O_4$ (801)	31.44 31.46	1.10 1.12	1.72 1.74	17.70 17.72)	-
								Br; Br;			39.91 39.95)

(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 benzoyl)-3-(substituted phenyl)tetrachlorophthalide:-. (G.F. = Green fluorescence)

Dyes	Colour in ethanol		Colour with 2%NaOH	λ_{max}(nm)		pH
	Neutral	alkaline		Neutral	alkaline	
13	Brown	pink	pink	510	530	9.4
14	Yellowish green	Dark red(G.F.)	Dark red	460	510	9.5
15	Light Brown	Dark Brown	Dark Brown	-	-	-
16	Brown	Yellowish brown	yellowish Brown	-	-	-
17	Brown	Bluish violet	violet	-	-	-
18	Yellow	Reddish orange	Reddish orange	-	-	-
19	Pinkish	Pink	Pink	-	-	-
20	Yellowish Pink	Pinkish red (G.F.)	Pinkish red (G.F.)	520	530	9.0

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

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^{0}C and then in vacuum desiccators, (3.0g, of the theoretical yield). The reddish brown microcrystalline dye having m. p.283-285^{0}Cis, soluble in benzene, ethanol, methanol and acetic acid. Its ethanolic solution is light yellow which alters to yellowish Orange with green fluorescence on adding a drop of an alkali. In strong basic medium, yellowish Orange color is obtained. Found: C, 51.80; H, 2.42; Cl, 29.18.% molecular weight 486 (Rast). Calcd for $C_{21}H_{32}Cl_4O_5$ C, 51.85; H, 2.47;Cl, 29.22.The preparation of rest of the dyes , given in table 1 has been done in the identical manner as already described.

4.3 ***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), 0.93 phenolphthalein, 0.91 .

4.4 ***Acetylation of dye (14)*** The dye 3-((2'amino, 4'methyl benzoyl)-3-(2, 4, di hydroxy phenyl) tetra chlorophthalide (1.0g) was refluxed with acetic anhydride (15 ml) at 130-140^{0}C for 4 h to give buff colouredmicro crystalline tri acetyl derivative (0.65g), mp, 132-134^{0}C (from rectified ethanol).It is soluble in ethanol, acetone, and acetic acid .Found: C, 53.02;H, 3.08;Acetyl, 21.09 calcd for $C_{27}H_{10}NCl_4O_4(OCCH_3)_3$: C, 53.02;H, 3.10; Acetyl, 21.11%.

4.5*Brominationof dye (14):-*The dye (15) (1.0g) and 10% solution of bromine in glacial acetic acid (10ml) were refluxed at 125-135^{0}C for 1 h. The contents were cooled and diluted with minimum quantity of distilled water. A brownish red powder di bromo compound (0.80g), mp, 130-135^{0}C Its ethanol solution is yellowish orange which turns into reddish orange with green fluorescence on addition of alkali. Found Br, 39.91;calcd for: $C_{21}H_9NCl_4Br_4O_4$; Br, 39.95.

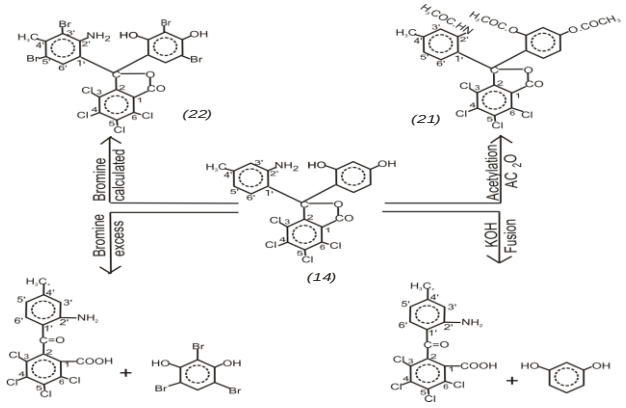
4.6 Caustic potash fusion of Dye (14)

Potassium hydroxide pallets (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) tetra chloro benzoic acid and confirmed by mixed melting point determination (m.p.228-230^{0}C) and by superimposition of the IR spectra of the authentic sample.

Residue-III:-The purified sample melted at 108-110^{0}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.



Scheme 2

5. Conclusion

We can therefore safely conclude that the color of resorcinol tetra chlorophthalide can be rationalized both in the solid state (reddish brown) and in neutral medium (**λ** -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 (460-510nm) in neutral medium. However, in slightly alkaline medium the **λ**max are shifted to the range of (510-530nm).

6. Acknowledgement

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