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Studies of Colour of Some Advanced Parallel of 3-(Naphthoyl)-3-(Substituted Phenyl) Phthalide

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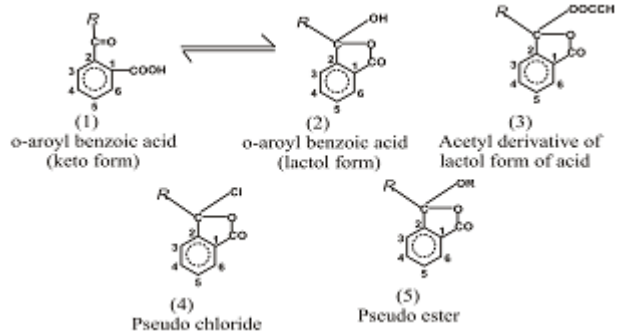
Abstract: ***Some advance dyes have been synthesized by condensation 2-(naphthoyl) benzoic acid with various phenol such as mono, di and tri hydric phenol using concentrated sulphuric acid as the condensing agent. The resulting compounds are substituted phthalides having central tri phenyl methane asymmetrical carbon atom attached to different phenyl rings such as 3-(naphthoyl)-3-(phydroxy phenyl)phthalide,3-(naphthoyl)-3-(2,4-dihydroxyphenyl) phthalide,3-(naphthoyl)-3-(2,3-dihydroxy phenyl) phthalide,3-(naphthoyl)-3-(2,5-dihydroxy phenyl) phthalide,3-(naphthoyl)-3-(2,3,4-trihydroxy phenyl) phthalide and 3-(naphthoyl)-3-(2,4,6-trihydroxy phenyl) phthalide. . The absorption spectra properties of as prepared phthalides were investigated in 95% Ethanol, attempt to evaluate spectral behaviors. The λmax and colour of some selected Innovative synthesized phthalide are observed in altered solvents having dissimilar colour.***

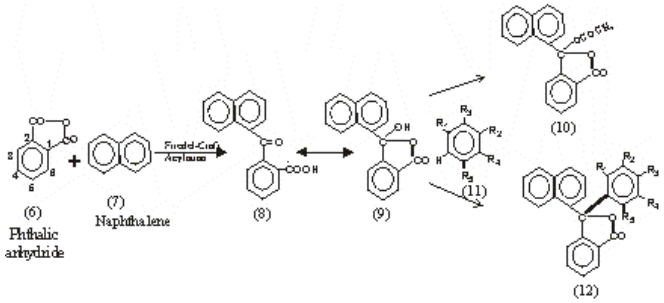
Keywords: Naphthoyl, Phenyl, Phenol, Resorcinol, Pyrrogallol, phloroglucinol

1. Introduction

Advanced Parallel of phthalide, 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 phthalide. In order to achieve this objective, phthalic anhydride is to be replaced by a properly substituted g-keto acid.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.[26] So on acetylation these lactol form of (2) to forms white crystalline acetyl derivative (3).[1] The ring isomer of gama keto acid are also forms pseudo chloride (4) [28] and pseudo ester (5)[2-3]. Many other workers [4-5] suggest that the gama keto acid have been explained on the basis of their cyclization to lactol. IR[6], Raman and NMR[34] spectra have been confirmed lactol form of the gama keto acid. The formation of 2-(naphthoyl) benzoic acid (7) from the substitution R of the cyclic or lactol form of gama keto acid by naphthalene and its acetyl derivative (10) 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 (naphthoyl) benzoic acid (7).



In this work the dyes prepared from the acid 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-(naphthoyl) benzoic 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 1682,1710,1735 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 2640cm^{-1} (week), 3100 (broad) cm^{-1}. In the NMR spectrum of the acid showed the general peaks at δ 1.5-2.6 m ,4.35 br due to 11, aromatic protons and lactol protons respectively.

IR spectrum of the acetyl derivative of the acid shows notable absorption band at 1680 cm^{-1}which may be assigned lactonic >C=O. peaks at 1760,1240,1210,1020 are due to presence of acetate groups. Peaks presence in the IR spectrum of the acid at 3100, 2640, 1682, 1710 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 1.65-2.8 m, 7.65 s due to 11and 3 protons of aromatic, and (-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-(naphthoyl) benzoic acid (9) of acid (8) with phenols (13) 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-(naphthoyl)-3-(2,4,di hydroxy phenyl) phthalide (14) having molecular formula $C_{24}H_{16}O_4$ molecular weight 368 ,

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	Acetyl
13	P-Hydroxy	160-180	6	Brown	122 Decomp	$C_{24}H_{16}O_3$ (352)	81.82 (81.65)	4.54 (4.50)	-
14	2.4-Dihydroxy	140-160	4	Dark red	280-282	$C_{24}H_{16}O_4$ (368)	78.26 (78.05)	4.34 (4.28)	-
15	2.3-Dihydroxy	120-130	3	Black	>300	$C_{24}H_{16}O_4$ (368)	78.26 (78.18)	4.34 (4.28)	-
16	2.5-Dihydroxy	165-180	4	Black	147-149	$C_{24}H_{16}O_4$ (368)	78.26 (78.10)	4.34 (4.25)	-
17	2,3,4-Tri hydroxy	130-140	5	Black	186-188	$C_{24}H_{16}O_5$ (384)	75.0 (74.82)	4.16 (4.08)	-
18	2,4,6-Tri hydroxy	210-220	4	Dark brown	260 Decomp	$C_{24}H_{16}O_5$ (384)	75.0 (74.76)	4.16 (4.05)	-
19	2,4-Di acetoxy	130-140	3½	Pale yellow	205-207	$C_{28}H_{20}O_6$ (452)	63.72 (63.65)	3.09 (3.02)	19.03 (19.08)
20	3,5-Dibromo 2,4-dihydroxy	120-125	1	Reddish orange	120-125	$C_{24}H_{14}O_4Br_2$ (526)	54.75 (54.60)	2.66 (2.50)	-
								Br; Br;	30.40 (30.55)

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

On acetylation yielded di acetyl derivative (19) indicating the presence of only two phenolic groups. When brominated with calculated amount of bromine, the dye gave a di 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-(naphthoyl) 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 phthalide are given in table (2).Table three shows the ($\boldsymbol{\lambda}_{max}$) true phthalide prepared in same. Absorption maxima of phthalide 11, 12 and 18 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, naphthalene, 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.

5.1-*Synthesis of 2-(naphthoyl) benzoic acid*

2-(naphthoyl) 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.

Table 2: Absorbtion maxima of 3-(*naphthoyl*)-3-(substituted phenyl phthalide:-. (G.F. = Green fluorescence)

Dyes	Colour in ethanol		Colour with 2%NaOH	λ_{max}(nm)		pH
	Neutral	alkaline		Neutral	alkaline	
13	Colourless	pink	Deep pink	510	530	8.6
14	Yellowish	Yellowish Orange(G.F.)	Yellowish Orange(G.F.)	460	500	9.5
15	Light Brown	Brownish	Black Brown	-	-	-
16	Brown	Light violet	Light yellow	-	-	-
17	Reddish Brown	violet	Blue black	-	-	-
18	Light Brown	Brown	Brown	-	490	8.8
19	Colourless	Yellowish (G.F.)	Yellowish (G.F.)	-	-	-
20	Yellowish Red	Yellowish Orange(G.F.)	Yellowish Orange(G.F.)	420	530	9

(-)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	λ_{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
Eosin	Light pink (G.F.)	Orange pink (G.F.)	Pink	530	530	10.5

5.2-*Synthesis of 3-(naphthoyl)-3-(2,4,di hydroxy phenyl) phthalide* (15):-

It was prepared by condensing an intimate mixture of the acid (8.0 g) and resorcinol (5.0g) in the oil bath in presence 5-6 drops of concentrated sulfuric acid at 140-160^{0}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^{0}C and then in vacuum desiccators, (6.5g,56% of the theoretical yield).The reddish brown microcrystalline dye having m. p.280-282^{0}C is, 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, 78.26; H, 4.34; % molecular weight 368 (Rast). Calcd for $C_{24}H_{16}O_4$ C,78.05; H,28;molecular weight 365.The preparation of rest of the dyes ,given in table 1 has been done in the identical manner as already described.

5.3 *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), 0.89 phenolphthalein,0.91 (lit [7] R_f 0.92).

5.4 Acetylation of dye (14)

The dye 3-(naphthoyl)-3-(2,4,di hydroxy phenyl) phthalide (1.0g) was refluxed with acetic anhydride (15 ml) at 130-140^{0}C for 4 h to give light yellow micro crystalline tri acetyl derivative (0.65g),mp,205-207^{0}C (from rectified ethanol).It is soluble in ethanol, acetone, and acetic acid . Found: C,63.72;H,3.09;Acetyl,19.03 calcd for $C_{24}H_{14}O_4$ $(OCCH_3)_2$: C,63.65;H,3.02; Acetyl,19.08%.

5.5 *Brominationof dye (14)*

The dye (15) (1.0g) and 10% solution of bromine in glacial acetic acid (10ml) were refluxed at 120-125^{0}C for 1 h. The contents were cooled and diluted with minimum quantity of distilled water. A brownish red powder di bromo compound (0.95g),mp, 276-278^{0}C Its ethanol solution is yellowish orange which turns into yellowish orange with green fluorescence on addition of alkali. Found Br, 48.23;calcd for: $C_{24}H_{14}O_4Br_2$; Br, 30.4.

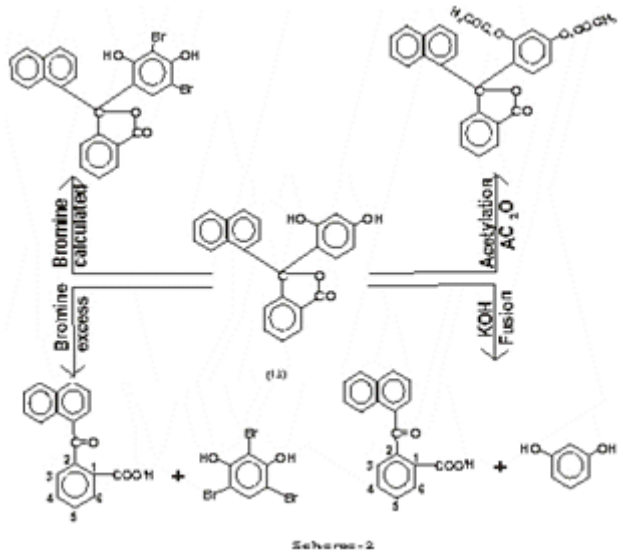
5.6 Caustic potash fusion of Dye (14)

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-(naphthoyl) benzoic acid and confirmed by mixed melting point determination (m.p.200-202^{0}C) and by superimposition of the IR spectra of the authentic sample.

Residue-III: The purified sample melted at 109-110^{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.



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 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 **λ**max are shifted to the range of (490-520nm).

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References

[1] P.R. Jones, "Ring chain tautomerisation.",Chem.Rev., Vol. 63, pp. 46-48, 1963.
[2] H.C.Martin,‹‹o benzoyl benzoyl chloride", J. Amer chem.Soc., vol,38,pp.1145,may 1916.
[3] M.S. Newman and C.D.Mc Cleary,"Normal and psudo ester of 2 benzoyl benzoic acid."J. Amer . chem. Soc., Vol, 63, pp.1537, 1941.
[4] P.M. Magnnity and T.J. glane, "The reaction of azomethines with methyl magnesium iodide" , J. Amer. chem. Soc., vol, 74, pp.4958-4959,oct 1952.
[5] Kuhn and H.Schretzmann,*chem, Ber*.,vol, 90, pp.457, jan1972.
[6] R. P. Chamoli,S.J.Rai, and P.C. Gupta, ‹‹Synthesis and Studies of some novel analogeus Phthalein Dyes," Bull Chemical Soc, Japan", Vol .53, pp.3000-3003,October 1980.
[7] R.Gopal and P.C.Gupta and S.P.Garg "Synthesis of succin-as-eins," Bullatin of the Chemical Soc Japan, Vol .47 no 7, pp.1789-1790,jul 1974.
[8] R.Gopal and P.C.Gupta, "Synthesis of succin-as-eins, Dyes derived from β-(2-Fluoroyl) propionic, β - (3-phenanthroyl) propionic and carbazol-3-6 bis (ϒ keto butyric acid)," Bullatin of the Chemical Soc Japan, Vol .48 no 7, pp.2227-2228, jul 1975.
[9] R.Gopal and P.C.Gupta and S.P.Garg, "Synthesis of Succin-as-eins,Dyes derived from β-benzoy propionic, β - (3-Acenaphthoyl)propioniand β-(α-Thenoyl)propionic Acids," Bullatin of the Chemical Soc Japan, Vol .47 no 7, pp.2027-2028,jul 1976.
[10] V. Kukreti and R. P. Chamoli, "Synthesis and spectra of some new phthalein dyes", Dyes and Pigments, vol.32, pp.15-24, September 1996.
[11] Ed. F. Degering, "Barnes & Noble series No. 6, organic Chemistry," Barnes and Noble, Inc. Ny., 1951, pp. 261.
[12] P.R. Jones and Stephen, L congdon ,‹‹Investigation of an abnormal organo cadmium reaction", J. Amer. chem. Soc., vol, 81, pp.4291-4294, aug 1959.
[13] Prokhorov, A.M. (Ed.) Handbook of Lasers (in two volumes), vol. I, sov. Radio,moscow, 1978, ch. 17, (in Russian).
[14] L.V. Tarasov,"Laser Physics, Translated from the Russian by R.S. Wadhwa," Mir publishers, moscow, pp, 30-36,1938.
[15] C. Decelles, "The story of Dye and Dyeing", (a senior student paper), J. chem. Educ. vol 26, pp.593-587, nov1949.
[16] H.E.Fierg- Davis and L. Biangly, "Fundamental processes of Dye chemistry'', interscience, New York, (1949).
[17] R.Venkataraman,"chemistry of synthetic Dyes", Academic press, New York, (1950).
[18] Bradley, "Recent progress in the chemistry of Dyes and Pigments", Roy. Inst. chem.Lectures, Monographs and Reports, 1958.
[19] F.M. Rowe, "The development of the chemistry of commercial synthetic Dyes''(1856-1938), Institute of chemistry, London (1958).
[20] O.H. Wheeter, "Near infrared spectra of organic compounds", chem. Rece, vol,59,pp.629-688, 1959.
[21] Stallman, "use of Metal complexes in organic, Dyes and Pigments." , J Chem. Educ. Vol,37, pp.220, may 1960,
[22] L.B. Lal, D.Phil. "Thesis on synthetic Dyes," Allahabad University, India, 1957.
[23] S.Ali , I.M.Beg and P.C. Gupta, "Synthesis and studies of some substituted Nitro phthal as eins", HCPB ,16, 1999.
[24] S.Ali. I.M. Beg.and P.C. Gupta, "Synthesis and studies of some mixed nitro and tetra chloro phthalides", by 36 Annual convention of chemists ORG(P) -158 , 1999.
[25] M.N.Beg,I.M.Beg,andDr.G.S. Nirajan.‹‹Synthesis & Physico chemical studies of some mixed nitro phthaleins", In National Seminar on recent development inchemistry of medicinal plant Dec. 2005. at D.B.S. College Kanpur.
[26] C. Decelles, 'The story of Dye and Dyeing', (a senior student paper), J. chem. Educ., vol 26, pp.593-587, (1949).
[27] H.E. Fierg- Davis and L. Biangly, 'Fundamental processes of Dye chemistry', interscience, New York, (1949).
[28] R.Venkataraman, 'chemistry of synthetic Dyes', Academic press, New York, (1950).

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