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Pyrrolo [2, 3-b] Naphth-4, 9-Dione Heterocyclic quinone Amino Acids as Novel Alternative Precursor in Phytopigment Like, Synthesis & Spectral Characterization

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Abstract

Reaction of 3-acetyl-2-amino-1, 4-naphthoquinone, and chloroacetic acid in the presence of ethanol/$NaHCO_3$ achieved 2-acetyl-3-glycenyl-1, 4 –naphtho quinone 52. On triturating of 52 under thermal piperidine, afforded 1-H-3-methyl pyrolo [2,3-b]-naphth-4, 9-dione-2-carboxylic acid **53**. Selective quaternization of **53** and phenacyl heterocyclic quaternary salts, achieved 2-carboxy-3-methyl pyrrolo [2, 3] naphth-4, 9-dione- 1[4(1)] α-substituted-3-monoazo- phytopigment like **$54_{a\text{-}e}$** The specific characterization of Heterocyclic pyrrolo [2, 3-b] naphth-4, 9-dione quinone amino acids precursors in phytopigment Like in colour are highly coloured compounds ranging from reddish brown to dark violet. The spectral behaviour of ethanolic solution of phytopigment Like in the visible region in order to permit a criterion for their use as photosensitizers. The solvatochromic behavior of phytopigment Like is observed here. The absorption spectra of phytopigment Like in different pure were examined in the visible region showing solvatochromism. This permits a selection of optimal solvent when such phytopigment Like is applied as photosensitizers. The spectral behavior of phytopigment Like in aqueous universal buffer solution and dissociation (protonation) constants (pka values) is described as a criteria for their use as photo-sensitizers and to permit their acido-baso chromic behaviour when is applied as photosensitizers

Key Words: Heterocyclic phytopigment like, synthesis, spectral, Solvato-(Media)-chromic Behaviour

INTRODUCTION

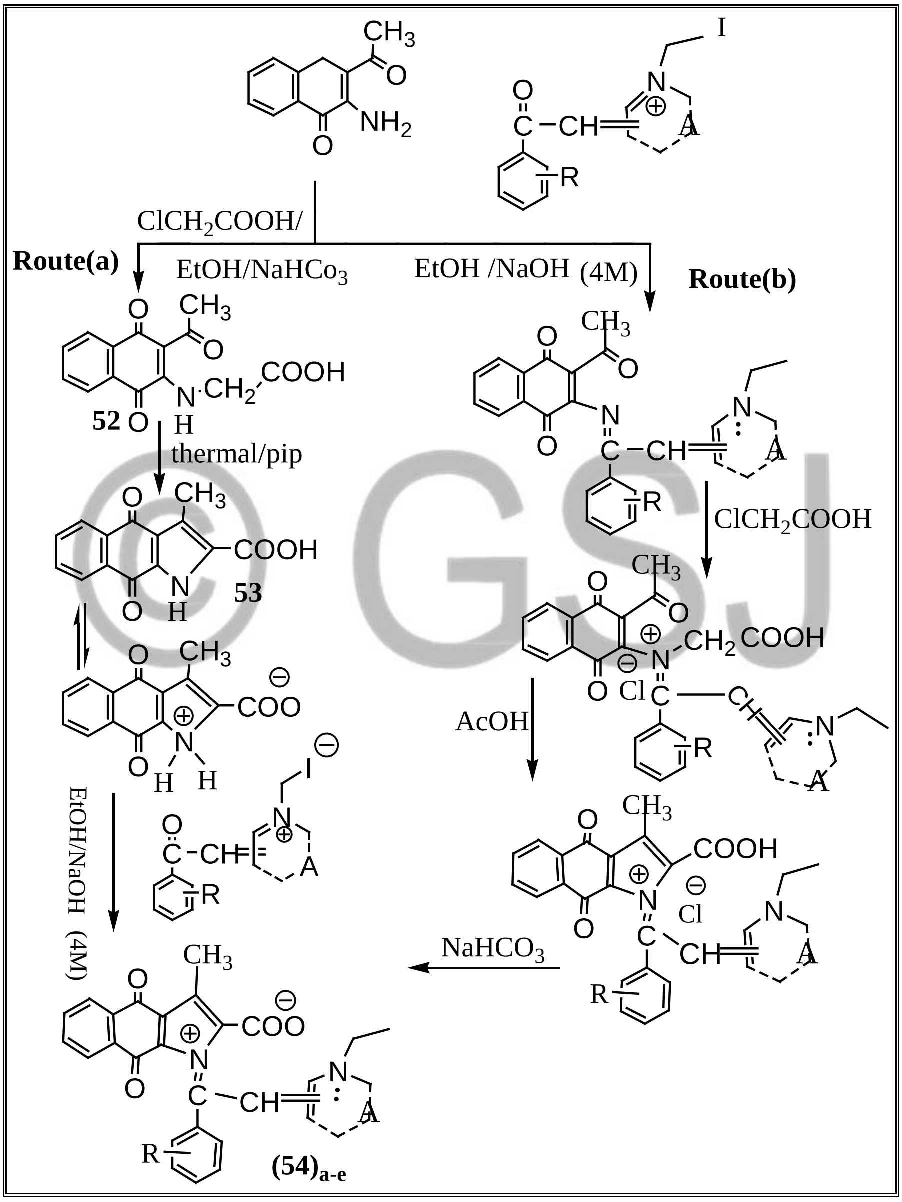
One of the main bottlenecks to the development of multi-property material is to pertain and search of new methodology for direct initial attempts for phytopigment synthesis. It is important to consider synthetic routes for facile and stable heterocyclic reagents and to produce the products in a good yield under the reaction conditions. There are several advantages in using other routes than conventional methods. Deeping the colour and increasing the intensity of spectral bands of such phytopigment like incorporating heterocyclic acid moieties is a criterion of photosensitization effect and play a dominant role in many biochemical systems as heterocyclic acids serve a central role in biology and chemistry being the fundamental constituents of proteins and mediators of nitrogen metabolism and provide raw material for a large number of biologically important primary and secondary metabolites **[1].** Pyrrolo [3,4-c] pyrazol-6-carbonyl-glycine carboxylic acid phytopigment like moieties have a little and no attention in the literatures The purpose of the present article is to evaluate an improvement of pyrrolo[3,4-c] pyrazol-6-carbonyl-glycine carboxylic acid nuclei & N-bridge head pyrimidine carboxylic acid phytopigment moieties as synthetic precursor's alternative entities to heterocyclic phytopigment like have a little and no attention in the literatures.

Recently, our approaches started to the synthesis of novel heterocyclic phytopigment like of pyrrolo[3,4-c]pyridazin-6-ium-7-carboxylate styryl tri-6[4(1)] methine phytopigment like**,** pyrazolo[4,3-e] pyrimido[1,6-c] pyrimidin-4-ium-5-carboxylate-4-phytopigment **&** pyrazolo [4,3-e]pyrimido [1,6-c]pyrimidin-4-ium-5-carboxylate-4-[α-Substituted-benzyl-idene]Styryl-phytopigment were prepared based on 5-acetyl-4-hydroxy-3-methyl-(3,4-dimethyl)-1-phenyl-1,3a,4,5-tetra[H] pyrrolo [3,4-c]pyrazol-6-carbonyl-glycine and pyrazolo[4,3-e]pyrimido[1,6-c] pyrimidin-6-ium-chloride/iodide **[2-6a,b]**

Results and Discussion

Synthesis:

Reaction of equimolar amounts of ethanolic solution 3-acetyl-2-amino-1, 4-naphthoquinone **[7],** and chloroacetic acid in the presence of sodium bicarbonate achieved 2-acetyl-3-glycenyl-1, 4 –naphtho quinone **52.** On triturating of such compound **52** under thermal piperidine afforded 1-H-3-methyl pyrrolo [2,3-b]-naphth-4, 9-dione-2-carboxylic acid **53.**The latter compound **53** was subjected to condense with phenacyl heterocyclic quaternary salts **[8],** to give 2-carboxy-3-methyl pyrrolo [2, 3-b] naphth-4, 9-dione-1 [4(1)] phytopigment like **54_{a-e}, Route (a).** The synthesis of **54_{a-e}** was confirmed chemically by direct interaction between 3-acetyl-2-amino-1, 4-naphthoquinone and phenacyl heterocyclic quaternary salts in the presence NaOH (4M) flowingly reacted with chloroacetic acid in ethanol to give the corresponding heterocyclic quinone ylide salts which under thermal undergoes ring closer, then treatment by $NaHCO_3$ to give the same dyes **54_{a-e}. Route (b), Scheme (1).**



Scheme (1)

<u>Scheme 1 Substituents:</u>

54_{a-e}: R=H, A=N-Ethyl-pyridine-4-yl (a); R=H, A= N-Ethyl -quinoline-4-yl (b);R=H, A= N-Ethyl -isoquinoline-1-yl (c);R=P.NH_2, A= N-Ethyl -isoquinoline-1-yl(d);R=P.NO_2, A= N-Ethyl -isoquinoline-1-yl (e).

The structure of **52, 53, 54_{a-e}** was confirmed by elemental analysis, **Table 4** and spectral analysis**.** IR (v^{KBr}) spectra of **52, 53** showed general absorption bands at 760-921cm^{-1} (v^{max} mono substituted aromatic), 1670-1766cm^{-1} (v, C= O), 3320-3481 (OH) **[9].**The ^{1}H-NMR(DMSO) spectra of **54_a** reveals signals at δ1.9ppm (s, 3H, of CH_3 ethiodide) at δppm (s, 5H, 2H, CH_2 ethiodide, 3H, CH_3) at 7.5-8.7 ppm (m, 14H, 13H, Ar-H, 2H,CH methine) **[10, 11].**

Colour nd Spectral Behaviour

Pyrrolo [2, 3-b] naphth-4, 9-dione-1 [4(1)] phytopigment like **54_{a-e}** is easily soluble in polar organic solvents and concentrated sulphuric acid from the iodine vapor was not liberated on warming. In 95%ethanol possess (dark brown to reddish brown), in colour. Their ethanolic solutions exhibited permanent coloured in basic media which reversibly discharged on acidification **Table 2*.*** The absorption spectra of Pyrrolo [2, 3-b] naphth-4, 9-dione-1 [4(1)] phytopigment like **54_{a-e}** in 95%ethanol consists of different absorption bands, their position and molar extinction coefficient being influenced by the type of heterocyclic quaternary residue (A) and nature of aryl substituents (R), Thus, the absorption spectra of **54_a** (R=H, A= pyridin-4-ium ethiodide) exhibit (λ_{max} = 445, 650nm; ε_{max} = 2079, 618 mol^{-1}cm^2). Substituting in **54_b**, (A=quinolinium-4- ium ethiodide), exhibit (λ_{max} = 460, 660 nm. ε_{max}= 2390 mol^{-1}cm^2) causes bathochromic shift due to the more extensive π-delocalization or conjugation in dye **54_a**. Changing the linkage position of quinoline residue from 4-ium in dye **54_b** [A= quinolinium-4- ium ethiodide] to 1- ium in dye **54_c** [R=H, A=quinolinium-4- ium ethiodide] resulted in bathochromic shift in absorption band exhibited (λ_{max} = 455, 655nm; ε_{max} = 2251, 614 mol^{-1}cm^2).On comparison of the absorption spectra between **54_c** and **54_d,** Z= P.NH_2 , A= isoquinolinium-1- ium ethiodide), bathochromic shift in absorption band exhibit **54_d**, λ_{max}= 475, 665nm. ε_{max}= 2776, 663 mol^{-1}cm^2).This is due to increase in electron donating of phenyl group causes an easier charge transfer towards the heterocyclic quaternary residue (A) as electron sink. Additionally, substituted **54_e**, R=4-NO_2, A= isoquinolinium-1- ium ethiodide) as electron withdrawing character in dye **54_e** gives hypsochromic shift of 10 nm. than those of the electron donating character accompanied with decreasing in the number of the absorption bands **54_e**, λ_{max} = 465, 665nm; ε_{max} = 2456, 722 mol^{-1}cm^2), causes decreasing in the charge transfer from aryl as electron source towards the heterocyclic quaternary residue (A) as electron sink **Table 4, Fig.(1) .**

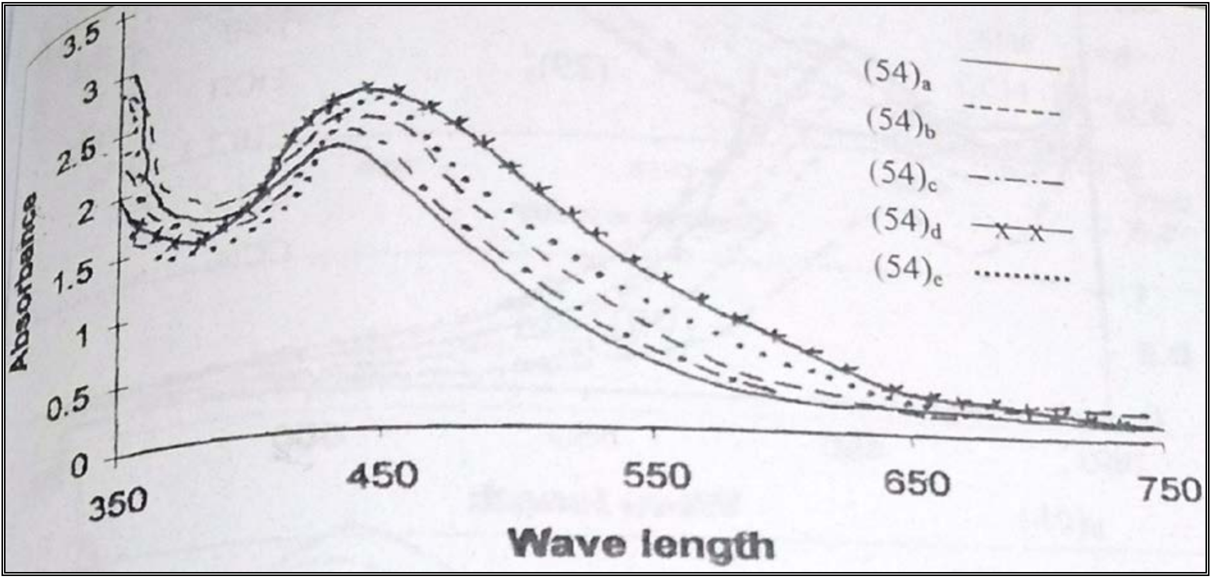


Fig.(1) Absorption spectra of Pyrrolo [2, 3-b] naphth-4, 9-dione-1 [4(1)] phytopigment like 54_{a-e} in 95%ethanol

Solvatochromic Behaviour of Pyrrolo [2, 3-b] Naphth-4, 9-Dione quinone Phytopigment Like (54_d)

2-Carboxy-3-methyl-pyrrolo [2,3]naphth-4,9-dione-phytopigment like **54_d.** The absorption spectra of the cited **54_d**, in the wavelength range 350-700 nm, have been studied in different organic solvents **(DMF, EtOH, $CHCl_3$, C_6H_6 & carbon tetrachloride) [14],** respectively. The colour changes of pyrrolo [2, 3-b] naphth-4, 9-dione-1 [4(1)] phytopigment like **54_{a-e}** with solvents having different polarities are presented in **Table 2.** This is constructed with the intention to illustrate the solvatochromic behaviour of such phytopigment like **54_{a-e}** (λ_{max} and ε_{max}) values of the intermolecular charge transfer bands are given in **Table 3**. Pyrrolo [2, 3-b] naphth-4, 9-dione-1 [4(1)] phytopigment like **54_{a-e}** showed positive solvatochromism with increased solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of phytopigment like are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This behavior occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which lead to formation of specific solvated forms of dyes. In point view of light absorption, it was obvious that most of the phytopigment like **54_d**, are absorbed the fundamental light absorption (reddish violet- red) as they have got absorption values in the range 400-545nm **Table 3, Fig.(2)** in accordance with the literature´s observations **[15-20]**. The selected phytopigment like might be suggested to be used as photosensitizers in most polar and non-polar organic solvents in the (reddish violet-red). Thus, it was obvious that phytopigment like **54_d** absorbed violet light in benzene, carbon tetrachloride, λ_{max} = 445-455 nm extended and improved to the absorption of blue light in DMF, EtOH, $CHCl_3$ and λ_{max} = 460- 470 nm.

Table 1: The characterized colour of (54_d) in organic solvents

Comp. No.	DMF	EtOH	$CHCl_3$	C_6H_6	CCl_4	Alcoholic solution in H_2SO_4	Alcoholic solution in NaOH
54_d	Reddish brown	Reddish brown	Brown	Pale Brown	Pale Brown	Brown	Dark brown

Table 2: Values of absorption (nm) and extinction coefficients ($mol^{-1}cm^{-1}$) of Pyrrolo [2, 3-b] Naphth-4, 9-Dione quinone Phytopigment Like (54_d) in pure organic solvents

Comp. No.	DMF		EtOH		$CHCL_3$		C_6H_6		CCl_4	
	λ_{max}	ε_{max}	λ_{max}	E_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	E_{max}
54_d	475	2268	475	2640	460	2.100	455	2.376	455	2.502

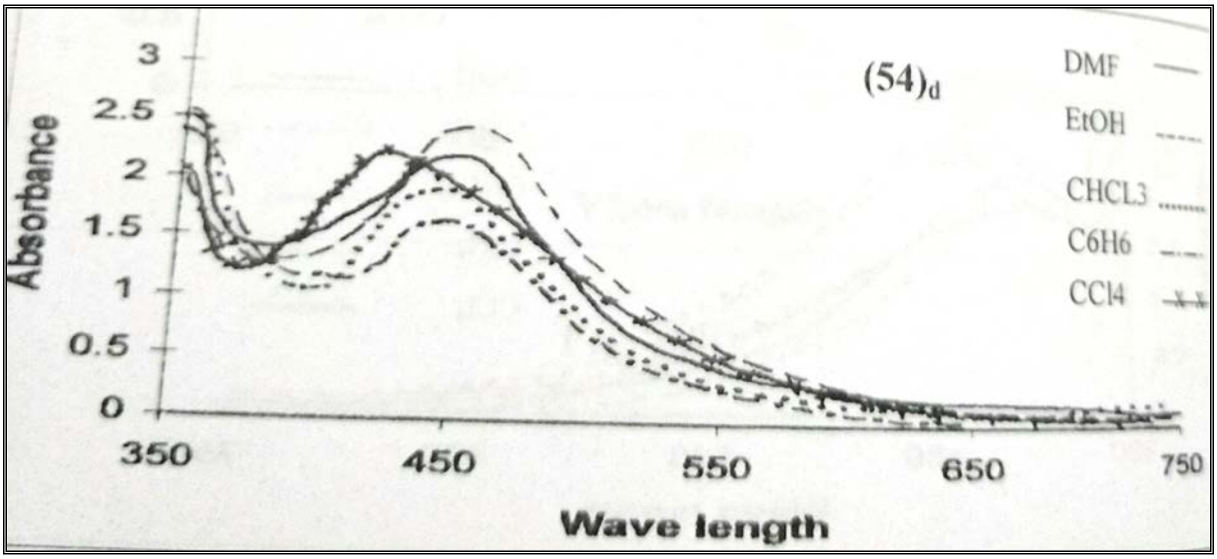


Fig.(2) Absorption spectra of 54_d, in the wavelength range 350-700 nm in different organic solvents

Media chromic Behavior and Acid-Base properties of Pyrrolo [2, 3-b] Naphth-4, 9-Dione quinone Phytopigment Like (54_d)

The ethanolic solution of phyto pigment cyanine dye like $\mathbf{54_b}$ give a permanent colour in basic medium which is discharged on acidification. This promoted us to study their spectral behavior in different aqueous universal buffer solution in order to ensure optimal pH in the application of these dyes as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic forms (non-protonated form) which have higher planarity **[21]**. The ethanolic absorption spectra of phytopigment like $\mathbf{54_b}$ in aqueous universal buffer solution of different values of pH (3.08 -10.02) show regular changes with increasing pH of the medium especially in the n-π^* and CT bands**.** The spectral behavior of $\mathbf{54_b}$ in 95% ethanol and/or in aqueous universal buffer solution showed that phytopigment like absorbed the near blue light extended to blue light λ_{max} = 460 – 480nm. for $\mathbf{54_b}$. Such phytopigment like in aqueous universal buffer solution reveals absorption of the violet light $\mathbf{(54)_b}$ at pH = 3.08 with hypsochromic and bathochromic shifted in the absorption of blue light λ_{max} = 480 nm. for $\mathbf{54_b}$ at pH ≥ 7.0 relative to ethanol. The hypsochromic shift of the violet light at pH = 3.08 is due to the presence of quinolinium ethiodide as strong inductively group causes the protonation of nitrogen atom in such solution of low pH value and therefore the interaction is inhibited and the protonated form does not absorb energy in the visible region. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to the fact that the protonated compound becomes deprotonated and therefore its mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction within the free base is facilitated, **Table 3, Fig. (3).** The spectrophotometric determination of dissociation and protonation constants pKa values of such phytopigment like $\mathbf{54_b}$ can be utilized through the variation of the absorbance with pH values **[22]**. Thus, the absorbance pH curves are typical dissociation constant pKa of the compounds were determined from the variation of absorbance with pH using the spectrometric half-height limiting absorbance and collector methods, **[*23, 24 and* 25].** The determination of pKa values of $\mathbf{54_b}$ were listed in **Table 3 Fig. (3),.** The results showed that the pKa values of $\mathbf{54_b}$ depend upon the nature of such phytopigment like type. Thus, the pKa values of $\mathbf{54_b}$ (phyto-pigment like dye) which contains quinolinium heterocyclic quaternary residue reveals pKa = 4.6 and 8.2. These results were suggested that the dye **54_b** are more sensititive as photosensitizers in both acidic and basic mediums and causes the high planarity in acidic and basic mediums.

Table (3): characterization of absorption value of 54_b in universal buffers.

EtOH pH	54_d		
	λ_{max}	ε_{max}	Abs.
	460	264	2.640
3.08	465	2918	2.918
4.2	465	2880	2.880
6.04	470	2959	2.959
7.64	475	2944	2.944
8.17	470	1599	1.599
10.02	480	2293	2.293
pKa	4.6		8.2

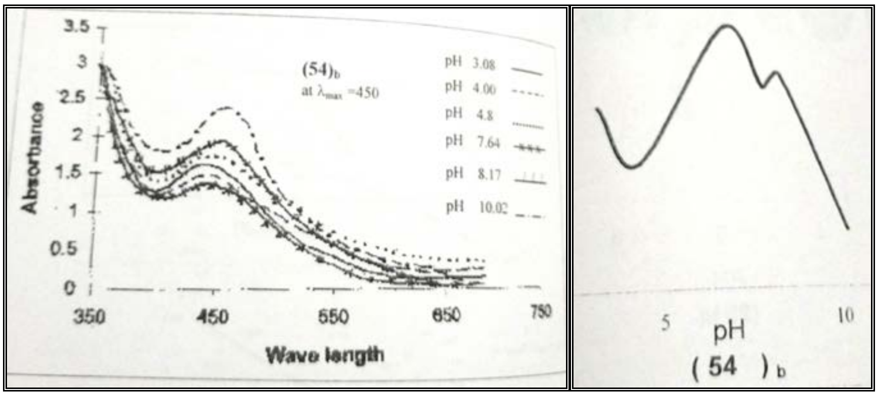


Fig.(3) Absorption value of 54_b in universal buffers.

EXPERIMENTAL

All melting points were uncorrected. IR spectra (KBr) were recorded on a pye Unicam SP1100 spectrophotometer. ^{1}H-NMR spectra were recorded in a Varian EM -390 MH_Z spectrophotometry using DMSO d_6 as a solvent and TMs as an internal standard. Chemical shift are expressed as ppm, units. Mass spectra were recorded on a HP Ms 6988 spectrometer and analytical data were determined with a CE 440 Elemental Analyzer- Automatic Injector at Cairo University. The electronic absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350-800nm) on a 6405 UV/ visible recording spectrophotometer, Aswan faculty of science at 27C^{o}. Ethanol (95%, ethanol- water 95:5 v/v) was used. pH was measured on a radelkis OP-208 pH-meter with universal buffer solution. The concentration of the stock solution was about 1x10^{-3} and the lower moralities were obtained by accurate dilution.

Synthesis of 2-carboxy-3-methyl pyrrolo [2, 3] naphth-4, 9-dione-1 [4(1)]-3-monoazo- phytopigment like 54$_{a-e}$

An ethanolic solution of 3-acetyl-2-amino-1, 4- naphtho quinone, **[7]** (0.01mol) and chloroacetic acid (0.01mol)) in the presence of piperidine was refluxed for 2-4 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with HCl acid. The precipitated product after dilution with water were separated, filtrated, crystallized from ethanol, afforded 2-acetyl-3-glycenyl-1,4–naphtho quinone **52**. **52:** m.p= 200-202 ^{o}C, yield = 58%, colour =reddish brown, Molecular formula = $C_{14}H_{11}NO_4$ (257),Calc. (found): C= 65.36 (65.40) H= 4.28 (4.20) N= 5.44(5.44). Compound **52** was fused under thermal piperidine for about 2-3 mint then add 25ml of ethanol as solvent and refluxed for 4-6 hours, filtered hot, concentrated, cooled and the product was precipitated on dilution with water and crystallized from ethanol to give 1[H]-3-methyl pyrolo [2,3-b]-napht-4, 9 dione-2 carboxylic acid **53.** m.p= 210-212 ^{o}c, yield = 48%, colour = dark reddish brown, Molecular formula = $C_{14}H_9NO_3$ (239), Calc. (found): C= 70.29(70.35) H= 3.8 (3.8) N= 5.85(5.84). An ethanolic solution of **53** $^{(}$0.01mol) and phenacyl heterocyclic quaternary salts, **[11],** (0.01mol) in the presence of 4M sodium hydroxide, was refluxed for 4-6 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from the suitable solvent to afford **54$_{a-e}$ Table 4.**

Table 4: Characterization of pyrrolo [2, 3] naphth-4, 9-dione-1 [4(1)]-3-monoazo- phytopigment like 54 $_{a-e}$

Comp. No.	Nature of product			Mol. Formula (M.Wt)	Calc.(Found)			Absorption spectra in 95% EtOH	
	Colour	m.p. °C	Yield %		C	H	N	λ_{max} n. m	E_{max} Mol $^{-1}$cm^{2}
54$_a$	Brown	200202	45	$C_{29}H_{23}N_2O_4Cl$ (498.5)	69.80 (69.87)	4.61 (4.68)	5.61 (5.67)	445	2079
54$_b$	Reddish brown	218220	56	$C_{33}H_{25}N_2O_4Cl$ (548.5)	72.19 (72.16)	4.55 (4.59)	5.10 (5.17)	460	2390
54$_c$	Brownish red	222	53	$C_{33}H_{25}N_2O_4Cl$ (548.5)	72.19 (72.16)	4.55 (4.59)	5.10 (5.17)	455	2251
54$_d$	Reddish brown	238240	59	$C_{33}H_{26}N_3O_4Cl$ (563.5)	70.27 (70.21)	4.43 (4.43)	7.45 (7.40)	475	2776
54$_e$	Brownish red	>250	63	$C_{33}H_{23}N_3O_6Cl$ (579.5)	68.33 (68.39)	3.96 (3.92)	7.24 (7.28)	465	2456

Solvatochromic and acid base properties:

The organic solvents were used of spectroscopic grade of purified according to the recommended methods **[12]**. The electronic absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 1-cm cell. The stock solution of the dye was of the order 10^{-3} M. Solution of low molarities used in spectral measurements was obtained by accurate dilution.

I- Preparation of phytopigment like Solution:

For studying the effect of pure solvents in the UV and visible range: An accurate volume of the stock solution of the dyes were diluted to appropriate volume in order to obtain the required concentrations. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect of time. For studying the spectral behaviour in mixed solvents in the visible region:
An accurate volume of the stock solution (10^{-3} M in ethanol) of the dyes were placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent. For studying the spectral behaviour in aqueous universal buffer solutions: An accurate volume of the stock solution was added to 5 ml of the buffer solution in 10-ml measuring flask, then completed to the mark with

redistilled water. The pH of such solution was checked before spectral measurements.

II- Preparation of Universal Buffer Solution:

A modified buffer series derived from that of **[13],** was prepared for use in the present investigation. The constituents are as follows: A solution of 0.4 M of each phosphoric and acetic acid was prepared by accurate dilution of A. R. concentrated stock. A solution of 0.4 M of boric acid was obtained by dissolving the appropriate weight of the recrystallized acid in redistilled water. A stock acid mixture was prepared by mixing equal volumes of three acids in large bottle. The total molarity of the acid was thus maintained at 0.4 M A series of buffer solutions with pH values ranging from (1.98-11.18) was prepared as recommended by **[13]**. This was done by mixing 150 ml of the acid mixture in a 250 ml measuring flask with the appropriate volume of 1.0 M NaOH and completed to the mark with redistilled water. This modification was performed in order to keep the ionic strength constant at all pH's mixed with different proportions of organic solvents used. The pH's of the buffer solutions were checked using Orion pH-meter model (60, A), accurate to ± 0.005 pH units, at 25 °C.

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