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Synthesis and Optical response to Acids and Leave this area blank for abstract info. Styryl Bases of a new _ Dihydro-**Benzo[a]phenazine** Chromophores Sharad R. Patil, Amol S. Choudhary and Nagaiyan Sekar* Department of Dyestuff Technology, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai - 400 019 (India). *E-mail: n.sekar@ictmumbai.edu.in, sharad.omd.patil@gmail.com OH OH EKOHPEperidine Ar H reflux, 3 h



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Synthesis and Optical Response to Acids and Bases of a New Styryl – Dihydro-Benzo[a]phenazine Chromophores

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ABSTRACT

Four novel styryl – dihydrobenzo[a]phenazine chromophores have been synthesized and spectroscopically characterized. They respond to acids and bases through changes in absorption resulting in strong bathochromic shift (> 437 nm). The emission quantum yields of the dyes were in the range 0.11 - 0.14. Computational studies have been performed to provide further insights into the nature of electronic transitions for the synthesized dyes. The qualitative trends observed in the optical properties, halochromism and geometrical isomers were supported by density functional theory (DFT) computations.

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Keywords: Dihydrobenzo[a]phenazines Halochromism pH sensor Stereochemistry

1. Introduction

Organic π – conjugated materials are increasingly gaining attention in many areas of chemistry and functional materials research.¹⁻⁷ The organic materials featuring donor – π – bridge – acceptor architecture have continued to attract wide attention owing to their potential applications in organic electronics such as red emitting charge transporters in Organic Light Emitting Diodes (OLEDs),⁸ Organic Field Effect Transistors (OFETs),⁹ sensitizers in excitonic solar cells (DSSCs),¹⁰ Organic Photovoltaics (OPVs),^{11, 12} and as highly sensitive chromophores in the area of molecular sensing.¹³

have electron -deficient Benzophenazine compounds characteristics. Hence, they are used in the design of n - typeorganic semiconductors; examples are pyrazinoquinoxaline derivatives, hexaazatriphenylenes, diquinoxalino, phenazine, and quinoxalino phenanthro phenazine.^{14, 15} Prachi Singh et al. synthesized some acidochromic derivative especially 5substituted amino benzo[a]phenazines form 1. 2 naphthoquinone and studied their solvatochromism and acidochromic properties.¹⁶ Halochromism is one of the key parameters that can be used to describe any processes and it provides valuable information about the progress of such processes. Indeed the phenazine core, which is highly π – deficient aromatic heterocycle, can be used as electron withdrawing part in push - pull structures for intramolecular charge transfer (ICT). ICT is a key parameter to obtain luminescent and non - linear optical (NLO) properties. Also, ICT is useful for the design principle and a push – pull π – electron system is usually required to separate substantial charges in order to perturb the receptor. ¹⁷

In this study, we designed and synthesized some new styryl substituted benzo[a]phenazine derivatives with different electron - donating abilities except nitro derivative (Scheme 1, chart 1). The substituent effects on their absorption spectra in solution were studied. However, to the best of our knowledge, the dihydrobenzo[a]phenazine derivatives containing naphthoquinone functionality have not been studied in detail for their optical sensor applications. In order to explore the feasibility, we have also investigated the sensitivity of these molecules toward acids and bases which could be considered as model studies. Both, acidic and basic environment modulate the intramolecular charge transfer depending on the donor and acceptor capabilities, resulting in significant changes of the electronic spectra. These external stimuli can be used to characterize local environments in artificial and biological materials, making compounds of this type interesting for sensing purposes. Chromophores changing color on interaction with acids and bases have been studied in detail in recent years owing to their importance in the sensor industry.

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Tetrahedron



Scheme 1. General synthetic scheme employed for the preparation of the Dyes (**5a-d**).



Chart 1. Structures of the Naphthoquinone fused Dihydrobenzo[a]phenazine Styryl dyes.

2. Results and discussions

2.1. Synthesis and Characterization

Synthesis of the dyes were accomplished by a two-step process as outlined in scheme 1, chart 1. In the first step, 2hydroxy, 1, 4-naphthoquinone (Lawsone) (1) was treated with the corresponding aldehydes (2a-d) in the presence of a catalytic amount of piperidine and ethanol at reflux temperature to yield 3substituted 1, 2, 4-triketo naphthoquinone styryl derivatives (3ad). To the best of our knowledge, the reactions of o – phenylenediamine (OPDA) with 1, 2 - naphthoquinone has not been explored. The o – phenylenediamine 4 was found to react in a facile manner with 1, 2 - naphthoquinone (3a-d). The substituted naphthoquinones were conveniently converted to dihydrobenzo[a]phenazines (5a-d) by refluxing with ophenylenediamine in AcOH/EtOH at 80 °C and subsequently reduced by Zn. The dyes were characterized by ${}^{1}H$ and ${}^{13}C$ – NMR, and mass spectral analysis. The dyes are yellow or brown in the solid state and freely soluble in common organic solvents.

2.2. Optical Properties

The UV-vis spectroscopic data of the dyes (**5a-d**) measured in THF solutions are displayed in **Figure 1** and the relevant parameters are compiled in **Table 1**. All the compounds exhibited a broad and moderately intense absorption band >400 nm attributable to the electronic transition originating from the π -molecular orbitals. The peak position of this band assumes a trend (**5a**< **5c**< **5b**< **5d**) reflecting the impact of the substituent on aldehyde segment on the electronic properties. They do not show solvatochromism and solvatofluorism significantly in the solvent environment used for measurement. The dyes **5b** and **5d** showed red shifted absorption profiles when compared to the dyes **5a** and **5c**. These observations cannot be explained by assuming charge transfer nature for the transition and the trend is not matching with the donor strength of the substituent on aldehyde segments (**Figure 1**). The red-shifted absorption

profiles observed for the dyes (**5b** and **5d**) is suggestive of the involvement of conjugative delocalization. The extended conjugation present in the above derivatives may lead to a red-shifted absorption. On the contrary, the blue – shifted profile observed for the dyes (**5a** and **5c**) may be attributed to the retardation of electronic delocalization caused by electron-withdrawing group. In view of these observations, it may be argued that the prominent absorption in the naphthoquinone derived styryl dyes is mainly originating from the $\pi - \pi^*$ transition.



Figure 1. Absorption spectra of the dyes (5a-d) recorded in THF.

Table 1. Optical data of the dyes 5a-d in THF^a

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Dye	$\lambda_{abs}(nm)$	log ɛ	$\lambda_{em}(nm)$	$\Delta\lambda(\text{cm}^{-1})$	• the main marked marked black		
5a	429	5.92	575	5919	0.11		
5b	446	5.84	667	7429	0.14		
5c	436	5.88	487	2402	0.03		
5d	450	5.94	577	4891	0.12		

^aAll spectra were recorded at room temperature at C = 1.0 X 10⁻⁶ M; $\lambda_{abs}(nm)$ = Maximum absorption wavelength in nm; $\lambda_{em}(nm)$ = Maximum emission wavelength in nm; $\Delta\lambda$ (nm) = Stokes shift in nm. ^bThe fluorescence quantum yield, measured at room temperature using fluorescein in 0.1 M NaOH (ϕ = 0.79) as a standard.

All the dyes displayed moderately intense emission in THF solutions (**Figure 2, Table 1**) when excited at their absorption maximum. The most blue-shifted emission profile was observed for the nitro derivative (**5c**) while the N, N – dimethylamino substituted derivative (**5b**) displayed a longer wavelength emission in THF solution. The dyes, **5a** and **5d** exhibited almost the same maximum wavelength of absorption in THF. The quantum yields were measured using fluorescein as reference standard.^{22, 23}The emission quantum yields of the dyes **5a**, **5b** and**5d** were 0.11, 0.14, 0.12 respectively, which were 4 times larger than that of dye **5c**. The relative fluorescence quantum yields are summarized for dyes **5a-d** in **Table 1**.



Figure 2. Normalized emission spectra of the dyes (5a-d) recorded in THF.

We demonstrated the ability of the dyes 5a-d to function as colorimetric and pH sensors due to basic character of nitrogen atoms of the phenazine ring and acidic character of the enolic proton. For this reason, we decided to study the effect of protonation and/or deprotonation on the optical properties of the synthesised dyes. The absorption spectra of the dyes bathochromically shifted on addition of trifluoroacetic acid (TFA) and triethylamine (TEA). The changes in the UV-vis spectra of 5a upon addition of trifluoroacetic acid (TFA) and triethylamine (TEA) are illustrated in Figure 3. The spectra show the progressive attenuation of the charge transfer absorption band for the neutral compound on increasing the concentration of acid, whereas a new red-shifted band corresponding to the protonated species appeared. This bathochromic shift is explained by an enhancement of the intramolecular charge transfer (ICT) within the molecule due to the increase in the electron-attracting character of the phenazine ring by protonation. The same trend observed, addition of TEA led to a new red-shifted band appeared (Figure 3). The bathochromic shift is possible that the deprotonation of phenolic hydrogen occurs in the presence of TEA and generates a strongly electron-accepting phenazine core.



Figure 3. Absorption spectra of the dye 5a measured for THF solutions with different amounts of TFA and TEA.

Table 2.	. Halochromic	effect of	the dyes	5a-d
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	$\lambda_{abs}(nm)$			$\Delta\lambda^a$	$\Delta \lambda^{b}$	$[\lambda_{abs}]^{c}$
Dye	Neutral	Acid	Base	(nm)	(nm)	(calc.)
	(THF)	(THF+TFA)	(THF+TEA)			(nm)
5a	429	455	488	+26	+59	538
5b	446	472	523	+26	+77	571
5c	436	437	487	+01	+51	558
5d	450	473	529	+23	+79	552

 $\Delta\lambda^a = \lambda_{abs} \ (THF+TFA) \ - \ \lambda_{abs} \ (THF); \ \Delta\lambda^b = \lambda_{abs} \ (THF+TEA) \ - \ \lambda_{abs} \ (THF); \ [\pmb{\lambda}_{abs}]^c = LUMO+1 \ to \ HOMO$

A representative illustration of changes for **5a-d** in the absorption profile on incremental addition of TFA and TEA is shown in **Table 2**. The halochromic properties of the dyes **5b**, **5c** and **5d** having similar trend to the dye **5a** (Figure S1-S3).As expected, the dye **5b**exhibits ared shift of their absorption bands upon protonation due to an increased charge transfer from the donors to the phenazinium moiety. This color change is fully reversible by neutralisation with a base triethylamine (TEA).

The red-shifted absorption peak realized for the dyes in the presence of TFA is attributed to the protonated species. It is possible that the protonation of phenazine segment occurs in the presence of TFA and generates a strongly electron-withdrawing phenazinium segment. Formation of phenazinium ion will trigger a facile intramolecular charge transfer between the N, N-dimethyl amino donor group and the phenazinium acceptor segment (Scheme 2). Addition of an excess TFA (1000 equiv) causes diprotonation leading to the formation of dictation "D". The formation of dictation "D" should completely remove the donoracceptor interactions in the molecule and the extinction of charge transfer transition. Second protonation leading to the species "C" or "D" for the dyes (5a-d) is unlikely as the remaining nitrogen's will become less basic after the monoprotonation due to the severe push-pull interaction (Scheme 2). The red-shifted absorption peak realized for the dyes in the presence of TEA is attributed to the negatively charged species. It is possible that the deprotonation of phenolic hydrogen occurs in the presence of TEA and generates a strongly electron-accepting phenazine core. Formation of phenazine anion will trigger a facile intramolecular charge transfer between the phenolic donor group and the phenazine acceptor segment (Scheme 3). The deprotonation of enolic hydrogen leading to the species "E" for the dyes 5a-d is the remaining nitrogen atoms will become more basic due to the severe push-pull interaction (Scheme 3).

This color change is fully reversible by neutralisation with acetic acid. On the basis of the above observations, it is believed that the dyes exhibit acid-base equilibria as illustrated in scheme 2 and scheme 3. The protonation was completed on the addition of 10 equivalent of TFA (Figure 3). The original color was regained by the addition of triethylamine which neutralizes the effect arising due to the addition of TFA. The observation of one or two isosbestic points suggests the presence of neutral and protonated forms in equilibrium and the latter being predominant at higher concentrations of TFA. On the basis of the above observations, it is believed that the dyes exhibit acid-base equilibria as illustrated in Scheme 2. Addition of an excess of TFA (1000 equiv) led to the bleaching of the color for 5a (Figure 3). The absorption pattern of 5c in the presence of excess TFA is significantly different from that observed for 5c in the absence of TFA. The appearance of weaker charge transfer transition at the very high wavelength.

2.3. Theoretical Calculation

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Scheme 2. Protonation equilibria of the dye **5b** in the presence of TFA.



Scheme 3. Deprotonation Equilibria of the Dye 5b in the Presence of TEA.

To unravel the structure-electronic property relationship in these molecules, we have performed DFT calculations as implemented in Gaussian 09 program package. We optimized the molecular structure of the dyes in the gas phase as well as in THF using B3LYP functional and 6-31G (d) basis set without any symmetry constraints. The optimized geometry was used for the electronic simulations where at least 10 electronic excitations were computed for each compound. According to DFT calculation, the dye 5b was found to exist as 'E' isomer (Figure 4). The lowest energy transitions derived from the theoretical analysis along with their vertical excitations from HOMO to LUMO+1 are listed in Table 2. According to TD - DFT calculation, as the protonation on phenazine ring gives red shifted absorption due to the electronic transition from HOMO to LUMO+1(Table 2, Figure 6). The electronic distributions in the HOMO and LUMO+1 for the dye 5b and their protonated and/or deprotonated forms (A, B, C, D, E) are shown in the Figure 5. The HOMO of this compound is delocalized over the N, N dimethylamine moiety, with maximum components arising from the nitrogen lone pair and/or from the π framework of the phenyl groups and is extended along the bridge to the central region of the molecule. In the LUMO orbital, which also has π – character, there is no significant contribution from the amine segment and electron density shifted toward the has the dihydrobenzo[a]phenazine moiety. In order to identify the effect of protonation on the optical properties, we have optimized the geometry of the protonated forms of the dye 5b also. Except for slight structural variations no significant alternations in the geometry were observed due to protonation. The HOMO of the dye 5b protonated forms A and B on protonation has shown a change in the electron distribution away from the dihydrobenzo[a]phenazine segment, while in the LUMO of the dye 5b protonated forms A and B the movement of electron density toward the dihydrobenzo[a]phenazine segment is noticed. However, no noteworthy changes in the electron distribution are observed for the HOMO and LUMO of the form C and D. All observations suggest that protonation these on the dihydrobenzo[a]phenazine segment enhances the electronaccepting ability and drifts the electron - density toward it and the effect is highly dependent on the donor strength of the N, Ndimethylamine. Higher wavelength vertical transitions were predicted for the protonated dyes, which is in agreement with the observed values. This indicates that the HUMO - LUMO transitions may be treated as $\pi - \pi^*$ transitions with prominent charge transfer contribution.



Figure 4. Optimized geometry of dye 5b.



Figure 5. Electronic distributions observed for the frontier molecular orbitals of the dye 5b and their protonated forms.



Figure 6. HOMO – LUMO+1 diagram of the dye **5b** protonated form B.

3. Conclusion

In conclusion, we have efficiently synthesised naphthoquinone fused dihydrobenzo[a]phenazine styryl dyes starting from 2hydroxy, 1, 4-naphthoquinone (Lawsone) (1) by employing simple addition and condensation reactions with the suitable aldehydes. The styryl dyes displayed rich optical properties in the ground and excited states. They do not displaysolvatochromism and solvatofluorism. But, these dyes exhibit halochromism. The linear absorption of the dyes 5a-d in the neutral, acidic and basic medium were investigated and they are all sensitive to the acidic/basic environment. Although the absorption spectra of the dyes were not influenced by the nature of the solvents, addition of TFA led to the preferential protonation of the phenazine segment. This has resulted in an interesting halochromism. The protonation with TFA and deprotonation with TEA result in strong bathochromic shifts of the absorption band. The relative fluorescence quantum yields of compounds were determined by using fluorescein in 0.1 M NaOH ($\phi = 0.79$) as a standard. Using DFT computations the red-shifted absorption peak observed for the dyes were identified to be originating from a π - π * transition with minor contribution from the charge transfer between the donor and acceptor fragments. The qualitative trends observed in the optical properties were supported by the theoretical computations pointing that the electronic structure in small molecules with weak donor-acceptor interactions can be modelled with accuracy using DFT computations. Photophysical properties of the compounds were supported by DFT and it was observed that computational results are good agreement with the DFT computations. The compounds were confirmed by IR, ¹H NMR, ${}^{13}\hat{C}$ NMR and mass spectral analysis. The research work described herein report naphthoquinone fused dihydrophenazine styryl derivatives. We hope that the naphthoquinone fused dihydrobenzo[a]phenazine styryl based fluorescent acid/base sensors will be developed and applied in sensor industry in the future.

4. Experimental Section

4.1. Physical measurements and Instrumentation

All analytical grade chemicals and reagents were procured from Sigma Aldrich (India) and were used without further purification. The reaction was monitored by TLC using 0.25 mm E – Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light.Purifications of all the compounds were

achieved by recrystallization. Melting points were measured on M standard melting point apparatus from Sunder industrial product Mumbai, and were uncorrected. The FTIR spectra were recorded on a JASCO 4100 Fourier Transform IR instrument (ATR accessories). The nuclear magnetic resonance spectra were recorded on a Varian 500 MHz instrument using CDCl₃ and DMSO-D₆ as a solvent and TMS as an internal standard. The chemical shift values are expressed in δ ppm. ESI – MS analysis was performed on Varian mass spectrometer. Hareus rapid analyser was used for elemental analysis. The UV - Vis spectra were performed with a Perkin - Elmer Lamda-25 spectrophotometer at room temperature. All solutions for energy transfer studies were prepared at the concentration of 1.0×10^{-6} M in THF and photophysical measurements were carried out.For the determination of emission quantum yields φ in THF, fluorescein in 0.1 M NaOH ($\varphi = 0.79$) was used as the reference standard.²², ²³The relative quantum yields of the synthesized compounds in THF solvents were calculated by using the equation (1).

$$\phi_{\rm x} = \Phi_{\rm st} \times ({\rm Grad}_{\rm X} / {\rm Grad}_{\rm st}) \times (\eta_{\rm X}^2 / \eta_{\rm st}^2)$$
(1)

Where,

 ϕ_x = Quantum yield of compound

 Φ_{st} = Quantum yield of standard sample

 $Grad_x = Gradient of compound$

 $Grad_{st} = Gradient of standard sample$

 η_x = Refractive index of solvent used for synthesized compound η_{st} = Refractive index of solvent used for standard sample

4.2. Computation Methods

The molecular geometries have been optimized using the Gaussian 09 suite of programs. ²⁴The ground state (S0) geometry of the dyes were optimized in the gas phase as well as in THF medium using DFT.²⁵The functional used was B3LYP. The B3LYP method combines Becke's three parameter exchange functional (B3)²⁶ with the nonlocal correlation functional by Lee, Yang and Parr (LYP). ²⁷ The basis set used for all atoms was 6-31G (d). The vibrational frequencies at the optimized structures were computed using the same method to verify that the optimized structures correspond to local minima on the energy surface. The vertical excitation energies and oscillator strengths were obtained for the lowest ten singlet-singlet transitions at the optimized ground state equilibrium geometries by using the Time Dependent Density Functional Theory (TD - DFT) with the same hybrid functional and basis set.²⁸⁻³⁰ Frequency calculations are carried out to ensure that each optimized conformation has all positive frequencies and thus is a minimum on the potential energy surface. The low-lying first singlet excited states (S1) of the dyes were relaxed using the TD - DFT to obtain their minimum energy geometries. We have done TD - DFT of the optimized first singlet excited state geometries for calculating the emission.³¹ Frequency computations were also carried out on the excited state geometry of the dyes. All the computations were carried out initially in gas phase and in acetonitrile solvent using the Self – Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM).^{32, 33} The electronic absorption spectra, including absorption wavelengths, oscillators strengths, and main configuration assignment, were systematically investigated using TD - DFT with PCM model on the basis of the optimized ground structures.

4.3. Synthesis and Characterisation

The synthesis of 3-benzylidenenaphthalene-1, 2, 4 (3H)-trione precursor (**3a-c**)has been described in our previous published paper. 34

4.3.1. Synthesis of 3-(2, 4-dimethoxybenzylidene)naphthalene-1,2,4(3H)-trione (3d)

A mixture of 2 – hydroxy – 1, 4 – naphthoquinone **1** (10 mmol), 2, 4 – dimethoxybenzaldehyde **2d**(10 mmol), and piperidine (2-3 drops) in ethanol was refluxed for 3 h.Progress of the reaction was monitored by TLC.The reaction mass was then poured into crushed ice. The precipitate solid obtain was filtered, washed with water and dried. Further purification was effected by recrystallization in methanol. Yield = (251 mg, 78%); M.p. = 248-250 °C; Rf (30% Hexane/EtOAc) 0.32; ¹H – NMR (CDCl₃, **500 MHz**) = δ 3.83 (s, 6H, OCH₃), 7.68-8.16 (m, 7H, aromatic), 9.75 (s, 1H, vinylic C=C-H); ¹³C-NMR (DMSO-D₆, 125 MHz) = δ 183.5, 180.1, 179.6, 165.7, 160.4, 151.2, 135.4, 134.9, 130.7, 128.5, 126.3, 114.1, 104.4;FT-IR (KBr, cm⁻¹) = 3056 (Ar-H), 1660 (C=O), 1590 (C=C), 1358 (C-O-C); Mass = *m*/z 322.99.

4.3.2. General procedure for Synthesis of (E)-6benzylidene-6, 12-dihydrobenzo[a]phenazin-5-ol derivatives (5a-d).

A solution of (E)-3-benzylidenenaphthalene-1, 2, 4(3H)-trione (**3a-d**) (10.0 mmol), o- phenylenediamine **4** (10.0 mmol), mixture of EtOH/AcOH(50:50) and pinch of Zn powder were heated at 80 °C. Progress of the reaction was monitored by TLC. On completion of the reaction, solvent (EtOH/AcOH) was removed by evaporation under reduced pressure in a rotary evaporator. The residue was poured into beaker containing crushed ice (80 mL) and agitated for 10 min. The precipitate obtainedwas filtered, washed thoroughly with water and dried. Further purification was effected by recrystallization in aq. DMF.

4.3.2.1. (E)-6-Benzylidene-6, 12dihydrobenzo[a]phenazin-5-ol derivatives (5a). Yield = (275 mg, 82%); M.p.= $270-272^{\circ}$ C;Rf (30%) Hexane/EtOAc) 0.69;¹H-NMR (DMSO-D₆, 500 MHz) = δ 16.37 (s, 1H, OH), 6.83-8.40 (m, 13H, aromatic), 6.15 (s, 1H, vinylic C=C-H), 3.80 (s, 1H, NH); ¹³C-NMR (DMSO-D₆, 125 MHz) = δ 160.1, 134.9, 134.8, 133.6, 132.3, 131.0, 130.9, 126.3, 125.9, 125.8, 111.4;FT-IR (KBr, cm⁻¹) = 3329 (OH), 3250 (NH), 3048 (Ar-H), 1665 (C=N), 1600 336.13.Anal. Calcd for (C=C); Mass = m/z C₂₃H₁₆N₂O (%): Calcd C, 82.12; H, 4.79; N, 8.33; O, 4.76. Found C, 82.61; H, 4.48; N, 8.35; O, 4.56.

4.3.2.2. (E)-6-(4-(dimethylamino)benzylidene)-6,12dihydrobenzo[a]phenazin-5-ol (**5b**).

Yield = (280 mg,74%); M.p.= 254-256 °C;Rf (30% Hexane/EtOAc) 0.62;¹H-NMR (DMSO-D₆, 500 MHz) = δ 16.34 (s, 1H, OH), 6.83-8.06 (m, 12H, aromatic), 6.15 (s, 1H, vinylic C=C-H), 3.84 (s, 1H, NH), 3.02 (s, 6H, NCH₃); ¹³C-NMR (DMSO-D₆, 125 MHz) = δ 156.7, 141.3, 135.1, 133.5, 132.6, 130.3, 128.5, 128.0, 126.4, 125.9, 125.8, 123.5, 48.6; FT-IR (KBr, cm⁻¹) = 3345 (OH), 3252 (NH), 3048 (Ar-H), 1664 (C=N), 1600 (C=C); Mass = m/z 379.33. Anal. Calcd for C₂₅H₂₁N₃O (%): Calcd C, 79.13; H, 5.58; N, 11.07; O, 4.22.Found C, 79.10; H, 5.48; N, 11.22; O, 4.20.

4.3.2.3. (E)-6-(4-nitrobenzylidene)-6, 12dihydrobenzo[a]phenazin-5-ol (5c). Yield = (289 mg,76% ; M.p.= 260-262 °C; Rf (30% M Hexane/EtOAc) 0.52; ¹H-NMR (CDCl₃, 500 MHz) = δ 11.84 (s, 1H, OH), 6.87-8.02 (m, 12H, aromatic), 6.16 (s, 1H, vinylic C=C-H), 3.42 (s, 1H, NH); ¹³C-NMR (DMSO-D₆, 125 MHz) = δ 143.6, 139.2, 135.2, 133.6, 132.4, 130.7, 128.3, 126.9, 126.5, 124.8, 124.4, 114.7; FT-IR (KBr, cm⁻¹) = 3378 (OH), 1537, 1420 (N=O), 1665 (C=O), 1600 (C=C);Mass = m/z 381.47.Anal. Calcd for C₂₃H₁₅N₃O₃ (%): Calcd C, 72.43; H, 3.96; N, 11.02; O, 12.59. Found: C, 72.22; H, 3.85; N, 11.51; O, 12.42.

4.3.2.4. (E)-6-(2,4-dimethoxybenzylidene)-6,12dihydrobenzo[a]phenazin-5-ol (5d). Yield **C** (340° mg, 86%); M.p.= 279-281 °C; Rf (30% Hexane/EtOAc) 0.59; ¹H-NMR (DMSO-D₆, 500 MHz) = δ 16.34 (s, 1H, OH), 7.63-8.65 (m, 12H, aromatic), 6.75(s, 1H, vinylic C=C-H), 4.25 (s, 1H, NH), 3.6 (s, 6H, OCH₃); ¹³C-NMR (DMSO-D₆, 125 MHz) = δ 164.8, 146.3, 135.9, 135.4, 134.1, 131.7, 131.2, 128.4, 127.5, 127.2, 126.7, 55.7; FT-IR (KBr, cm⁻¹) = 3056 (Ar-H), 1660 (C=O), 1590 (C=C), 1247 (C-O-C); Mass = m/z 395.60. Anal. Calcd for C₂₅H₂₀N₂O₃ (%): Calcd C, 75.74; H, 5.08; N, 7.07; O, 12.11. Found C, 75.64; H, 5.13; N, 7.11; O, 12.12.

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